A11102 136881

NAT'L INST OF STANDARDS & TECH R.I.C.

A11102136881

/Circular of the National Bureau of Stan
QC100 .U555 V510 C.1 NBS-PUB-C 1934

National Bureau of Standards
Library, N. W. Bldg.
AUG 1 9 1952

Copy 2

NBS CIRCULAR 510

# Tables of Chemical Kinetics

## Homogeneous Reactions

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

# Tables of Chemical Kinetics

## Homogeneous Reactions

These Tables are delivered in the form of punched loose sheets, temporarily assembled under a paper cover. This cover can be removed at the discretion of the subscriber upon receipt of a batch of supplementary sheets which can then be inserted at their right place as indicated by the number of the table, and the whole set can then be held in a suitable loose-leaf binder.

Each table is designated by a six-digit number, the first two of which refer to the type of reaction, the third to the phase of the homogeneous reaction, gaseous (1), liquid (2), or solid (3). The indication of the phase is repeated at the upper right-hand corner of the first sheet of each table. The second three-digit group of the table number refers to the types of substances involved. Within each table, reactions are numbered. In tables including more than one page, the table number is repeated at the head of each page, and the pages are numbered. Each table starts on a new sheet.

The first supplementary installment, to be delivered at a later stage, may include additional tables, additions to tables now delivered, and revised sheets canceling and replacing parts of the present tables. Such changes will be duly indicated on the new sheets. Further supplementary installments will be delivered at future dates as new or revised data material warrants it.

---

For sale by the Superintendent of Documents, United States Government Printing Office, Washington 25, D. C. Price $4.00.

UNITED STATES DEPARTMENT OF COMMERCE, Charles Sawyer, Secretary

NATIONAL BUREAU OF STANDARDS, E. U. Condon, Director

# Tables of Chemical Kinetics

## Homogeneous Reactions

**National Bureau of Standards**

E. U. Condon, Director

**National Research Council, Committee on Tables of Constants**

E. U. Condon, Chairman
H. S. Taylor, Vice-Chairman
E. R. Smith, Secretary
A. H. Emery
R. C. Gibbs
L. P. Hammett
W. A. Noyes
F. D. Rossini

**Editorial Office: Frick Chemical Laboratory, Princeton University**

N. Thon, Editor
D. G. Kelemen, Assistant
G. Parravano, Assistant
G. S. Forbes, Corresponding expert collaborator
M. Szwarc, Corresponding expert collaborator
H. A. Taylor, Corresponding expert collaborator

NATIONAL BUREAU OF STANDARDS LIBRARY NBS

Circular of the National Bureau of Standards 510

Issued September 28, 1951

## Foreword

The publication of International Critical Tables in 1926 provided the world with a comprehensive and critical selection of the then existing scientific data. Scientists of many nations cooperated in its compilation. Since then, the immense growth and refinement of scientific data have made much of it obsolete and incomplete, but its revision would be an enterprise even more tremendous than the original collection. A cooperative effort has therefore been established among the National Research Council, the International Union of Pure and Applied Chemistry, the International Union of Pure and Applied Physics, the National Bureau of Standards, and other interested institutions to compile separate critical tables of data in selected fields. The selection is governed by the apparent need in particular fields and the availability of experts thoroughly familiar with the subjects to undertake the work.

The tables presented in this volume represent one of these cooperative efforts sponsored by the National Bureau of Standards, the Committee on Tables of Constants of the National Research Council, and Princeton University.

E. U. Condon, *Director.*

National Bureau of Standards
MAY 1 0 1954
83883
QC100
.U555
cop.2

## Contents


| | Page |
|---|---|
| Foreword | II |
| Subject index | IV |
| Alphabetical index | XII |
| Code abbreviations for periodicals | XV |
| Introduction | XVII |
| Tables | 1 |

# SUBJECT INDEX

## 100 REARRANGEMENT - ISOMERIZATION


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 100 | ORTHO-PARA CONVERSION | | |
| | | Ortho-para conversion (gas) (4) | 101.000 |
| | | " " " (liquid) (4) | 102.000 |
| | | " " " (solid) (1) | 103.000 |
| 110 | RACEMIZATION | | |
| | *111* | *Racemization (gas)* | |
| | | Racemization; organic halogen compounds (1) | 111.470 |
| | *112* | *Racemization (liquid)* | |
| | | Racemization; C,H,O compounds (5) | 112.440 |
| | | " ; organic halogen compounds (2) | 112.470 |
| 120 | CIS-TRANS ISOMERIZATION | | |
| | *121* | *Cis-trans isomerization (gas)* | |
| | | Cis-trans isomerization; C,H,O compounds (2) | 121.440 |
| | | " " " C,H,N " (1) | 121.450 |
| | | " " " organic halogen compounds (1) | 121.470 |
| | *122* | *Cis-trans isomerization (liquid)* | |
| | | Cis-trans isomerization; C,H,O compounds (2) | 122.440 |
| | | " " " organic halogen " (1) | 122.470 |
| 130 | SYN-ANTI ISOMERIZATION | | |
| | *132* | *Syn-anti isomerization (liquid)* | |
| | | Syn-anti isomerization; C,H,O,N compounds, aromatic (1) | 132.452 |
| 140 | BRANCHING ISOMERIZATION | | |
| | | Branching isomerization; hydrocarbons (2) | 142.400 |
| 150 | ATOM (or GROUP) MIGRATION | | |
| | | Hydrogen migration (1) | 152.440 |
| | | Alkenyl group migration on aliphatic C (2) | 152.441 |
| | | " " " on alicyclic ring (1) | 152.443 |
| | | OH group migration (4) | 152.461 |
| | | H substitution by $NH_2$ from side chain (3) | 152.552 |

## SUBJECT INDEX *(continued)*


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 150 | **ATOM (or GROUP) MIGRATION** *(continued)* | | |
| | | H substitution by halogen from NX group in ring (2) | 152.752 |
| 160 | **POSITION EXCHANGE** | | |
| | | Beckmann rearrangement (3) | 162.455 |
| 170 | **RING CLOSURE** | | |
| | | Double bond to closed ring (2) | 172.441 |
| | | Ring-closing ionization (1) | 172.476 |
| 180 | **RING OPENING** | | |
| | | Ring opening to double bond (1) | 181.441 |
| 200 | **CONDENSATION-SOLVOLYSIS** | | |
| 200 | **ESTERIFICATION** | | |
| | *201* | *Esterification (gas)* | |
| | | Aliphatic acid anhydride + Alcohol (1) | 201.441 |
| | *202* | *Esterification (liquid)* | |
| | | Aliphatic carboxylic acid + Alcohol (19) | 202.441 |
| | | Aromatic " " + " (8) | 202.442 |
| | | Aliphatic alcohol + Hydrohalic acid (5) | 202.471 |
| | | " polyalcohol + " " (1) | 202.475 |
| 210 | **ESTER SOLVOLYSIS** | | |
| | *212* | *Ester Solvolysis (liquid)* | |
| | | Aliphatic carboxylic acid + Alcohol (18) | 212.441 |
| | | Aromatic " " + " (11) | 212.442 |
| | | Aliphatic " " + Phenol (4) | 212.443 |
| | | " " " + Polyalcohol (2) | 212.445 |
| | | " " polyacid + Alcohol (2) | 212.447 |
| | | Alkyl arylsulfonate (1) | 212.461 |
| | | Phenyl sulfate (2) | 212.463 |
| | | Aliphatic alcohol + Hydrohalic acid (39) | 212.471 |
| | | Aryl halide (1) | 212.473 |
| | | Alkyl halide + Phenolate (4) | 212.478 |
| | | Mercaptyl carboxylate (1) | 212.641 |
| 220 | **ESTER EXCHANGE** | | |
| | *222* | *Ester Exchange (liquid)* | |
| | | Aliphatic alcohol + Alkyl carboxylate (1) | 222.441 |
| | | " " + Phenyl " (3) | 222.443 |

## SUBJECT INDEX *(continued)*


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 220 | ESTER EXCHANGE *(continued)* | | |
| | | Alkyl halide + Carboxylic acid (3) | 222.471 |
| | | Alkyl carboxylate + Hydrohalic acid (2) | 222.741 |
| 230 | CONDENSATION | | |
| | *232* | *Condensation (liquid)* | |
| | | Aromatic aldehyde + Ketone (1) | 232.446 |
| | | C:N bond formation (10) | 232.451 |
| | | Aliphatic alcohol + Alkyl halide (4) | 232.471 |
| | | Phenol + " " (2) | 232.472 |
| 240 | NONESTER SOLVOLYSIS | | |
| | *242* | *Nonester Solvolysis (liquid)* | |
| | | Ether (2) | 242.441 |
| | | Acetal (3) | 242.442 |
| | | Acid anhydride (2) | 242.443 |
| | | C:N bond (2) | 242.451 |
| | | $CO-NH_2$ bond (Acylamide) (7) | 242.452 |
| | | C⋮N bond (13) | 242.453 |
| | | $C:N_2$ bond (9) | 242.455 |
| | | $C:N_2$ bond + aromatic carboxylic acid (2) | 242.456 |
| | | Aromatic acyl halide (4) | 242.472 |
| | | CN halide (1) | 242.570 |
| 250 | V th GROUP BOND SOLVOLYSIS | | |
| | | P - O bond (1) | 252.560 |
| 300 | EXCHANGE - SUBSTITUTION | | |
| 300 | ISOTOPIC EXCHANGE | | |
| | *302* | *Isotopic exchange (liquid)* | |
| | | H-D exchange on aliphatic C (3) | 302.401 |
| | | " " " aromatic C (2) | 302.402 |
| | | Oxygen isotope exchange (1) | 302.461 |
| | | Halogen isotope exchange (6) | 302.477 |
| 310 | HYDROGEN SUBSTITUTION | | |
| | *311* | *Hydrogen Substitution (gas)* | |
| | | H - S exchange on aliphatic C (1) | 311.460 |
| | | Hydrogen-Halogen-Hydrogen halide exchange (6) | 311.700 |
| | *312* | *Hydrogen Substitution (liquid)* | |
| | | Nitration of aromatic compounds (5) | 312.452 |
| | | Sulfonation of " " (1) | 312.462 |
| | | Halogenation on aliphatic C (17) | 312.471 |

## SUBJECT INDEX *(continued)*


| | | | Title of Table (number of pages) | Table number |
|---|---|---|---|---|
| 310 | HYDROGEN SUBSTITUTION *(continued)* | | | |
| | | | Halogenation on aromatic C (31) | 312.472 |
| 330 | EXCHANGE OF SUBSTITUENTS | | | |
| | *332* | | *Exchange of Substituents (liquid)* | |
| | | | $NO_3^-$ for halogen on aliphatic C (1) | 332.571 |
| | | | Halogen for $NO_3^-$ " " " (5) | 332.751 |
| | | | " " $NH_2(NR_2)$ on " " (3) | 332.755 |
| | | | " " " " " aromatic C (2) | 332.756 |
| | | | " " $S_2O_3^{--}$ " aliphatic C (6) | 332.761 |
| | | | " " halogen " " " (9) | 332.771 |
| | | | " " " " aromatic " (1) | 332.772 |
| | | | " " perhalate ion (1) | 332.776 |
| 350 | EXCHANGE ON V th GROUP ELEMENT | | | |
| | | | Halogen for H in CN halide (1) | 352.470 |
| | | | " " $NH_2(NR_2)$ in CN halide (1) | 352.475 |
| 380 | COORDINATIVE EXCHANGE | | | |
| | | | Halogen for $H_2O$ in VIII th group complex (1) | 382.870 |
| 400 | ELIMINATION | | | |
| 400 | PROTON ELIMINATION | | | |
| | | | $H^+$ from C - N bond (5) | 402.450 |
| 420 | BOND-UNSATURATION ELIMINATION | | | |
| | | | Hydrogen halide from C - C bond (9) | 422.471 |
| | | | " " " C - N bond (3) | 422.475 |
| | | | Halogen molecule by halide ion (3) | 422.477 |
| 430 | RING - CLOSURE ELIMINATION | | | |
| | | | Hydrogen halide from halohydrin (3) | 432.471 |
| 450 | ELIMINATION FROM V th GROUP ELEMENT | | | |
| | | | Hydrogen halide from quaternary base (3) | 452.471 |
| 460 | ELIMINATION FROM FUNCTIONAL GROUP | | | |
| | | | $CO_2$ from aliphatic COOH (1) | 462.441 |
| 500 | DISSOCIATION - DECOMPOSITION | | | |
| 500 | DISSOCIATION OF ASSOCIATED MOLECULES | | | |
| | | | Nitrogen oxides (1) | 501.562 |

## SUBJECT INDEX *(continued)*


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 510 | **MOLECULAR - COMPOUND DISSOCIATION** | | |
| | *511* | *Molecular-composed Dissociation (gas)* | |
| | | Dicarboxylate to Anhydride + Aldehyde (4) | 511.443 |
| | *512* | *Molecular-composed Dissociation (liquid)* | |
| | | Aldehyde hydrate (1) | 512.410 |
| | | Cyanohydrin (1) | 512.415 |
| | | Diacetone alcohol (4) | 512.441 |
| 520 | **BOND-UNSATURATION DECOMPOSITION** | | |
| | *521* | *Bond-unsaturation Decomposition (gas)* | |
| | | Loss of hydrogen halide (2) | 521.471 |
| | | " " halogen molecule (2) | 521.477 |
| | *522* | *Bond-unsaturation Decomposition (liquid)* | |
| | | Dehydration of organic compound (2) | 522.442 |
| | | Deamination " " " (1) | 522.451 |
| | | Desulfonation of " " (1) | 522.461 |
| 540 | **REDUCTIVE DECOMPOSITION** | | |
| | *541* | *Reductive Decomposition (gas)* | |
| | | Hydrogen peroxide (3) | 541.160 |
| | | Carbon oxyhalides (1) | 541.470 |
| | | Nitrogen oxides (6) | 541.560 |
| | | Ozone (2) | 541.660 |
| | | Halogen oxides (1) | 541.760 |
| | *542* | *Reductive Decomposition (liquid)* | |
| | | Nitrogen oxides (2) | 542.560 |
| | | Nitramide (5) | 542.561 |
| | | Ozone (3) | 542.660 |
| 560 | **DECOMPOSITION OF FUNCTIONAL GROUP** | | |
| | *561* | *Decomposition of functional group (gas)* | |
| | | $N_2$ evolution from azo compound (1) | 561.451 |
| | *562* | *Decomposition of functional group (liquid)* | |
| | | CO evolution from COOH (5) | 562.441 |
| | | $CO_2$ " from aliphatic mono-COOH (4) | 562.445 |
| | | " " " " di-COOH (7) | 562.446 |
| | | " " " aromatic COOH (3) | 562.447 |
| | | $N_2$ " " diazonium halide (3) | 562.457 |

## SUBJECT INDEX *(continued)*


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 570 | **PYROLYSIS** | | |
| | *571* | *Pyrolysis (gas)* | |
| | | Alphatic hydrocarbons (11) | 571.411 |
| | | Aromatic " (1) | 571.412 |
| | | Alicyclic " (1) | 571.413 |
| | | Aliphatic C,H,O compounds (15) | 571.441 |
| | | Aromatic " " (2) | 571.442 |
| | | Heterocyclic " " (1) | 571.444 |
| | | Aliphatic C,H,N " (5) | 571.451 |
| | | Aromatic nitro " (1) | 571.456 |
| | | Aliphatic halogen " (1) | 571.471 |
| 580 | **RING-OPENING DECOMPOSITION** | | |
| | | Alicyclic ring to Unsaturated compounds (1) | 581.441 |
| 600 | **ASSOCIATION - ADDITION** | | |
| 610 | **MOLECULAR ASSOCIATION** | | |
| | *611* | *Molecular association (gas)* | |
| | | Aldehyde + Anhydride → Dicarboxylate (1) | 611.443 |
| | *612* | *Molecular association (liquid)* | |
| | | Aldehyde hydration (1) | 612.410 |
| | | HCN to carbonyl (1) | 612.415 |
| 620 | **BOND SATURATION** | | |
| | *621* | *Bond Saturation (gas)* | |
| | | Hydrogenation of multiple bond (2) | 621.411 |
| | | Hydrogen halide to double bond (2) | 621.471 |
| | | Halogen molecule to " " (1) | 621.477 |
| | *622* | *Bond Saturation (liquid)* | |
| | | $H_2O$ to C:C bond (2) | 622.442 |
| | | $H_2O$ to C:C bond (1) | 622.443 |
| | | $H^+$ to C:N " (1) | 622.450 |
| | | Hydrogen halide to multiple bond (1) | 622.471 |
| | | Halogen molecule to " " (30) | 622.477 |
| 630 | **RING-OPENING ADDITION** | | |
| | | Ring opening by addition of $OH^-$ (2) | 632.441 |
| 640 | **OXIDATIVE ADDITION** | | |
| | | CO + Halogen (1) | 641.470 |
| | | N oxide + Oxygen (2) | 641.560 |
| | | N oxide + Halogen (2) | 641.570 |

## SUBJECT INDEX *(continued)*


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 650 | **QUATERNARY BASE FORMATION** | | |
| | *651* | *Quaternary base formation (gas)* | |
| | | Alkyl halide + Aliphatic amine (1) | 651.471 |
| | *652* | *Quaternary base formation (liquid)* | |
| | | Aliphatic acid ester + Amine (1) | 652.441 |
| | | Aromatic " " + " (1) | 652.442 |
| | | Alkyl halide + Aliphatic amine (5) | 652.471 |
| | | " " + Aromatic " (9) | 652.472 |
| | | Aromatic " + " " (1) | 652.474 |
| | | " acyl halide + Aromatic amine (2) | 652.476 |
| | | Alkyl halide + Heterocyclic amine (9) | 652.477 |
| 660 | **FUNCTIONAL GROUP ADDITION** | | |
| | | $SO_3$ to aromatic hydrocarbon (2) | 662.462 |
| 680 | **RING - CLOSURE ASSOCIATION** | | |
| | *681* | *Ring-closure association (gas)* | |
| | | Unsaturated compounds to alicyclic ring (2) | 681.441 |
| | *682* | *Ring-closure association(liquid)* | |
| | | Unsaturated compounds to alicyclic ring (1) | 682.441 |
| 700 | **OXIDATION - REDUCTION** | | |
| | | *Reactions are formulated with the reductant written first, the oxidant second.* | |
| 710 | **OXIDATION - REDUCTION DISMUTATION** | | |
| | | VI th group elements (2) | 712.660 |
| | | VII th " " (8) | 712.770 |
| 720 | **OXIDATION-REDUCTION, Compounds (ions) of the same element** | | |
| | | V th group elements (1) | 722.550 |
| | | VI th " " (1) | 722.660 |
| | | VII th " " (6) | 722.770 |
| 730 | **OXIDATION-REDUCTION, Compounds (ions) of different elements** | | |
| | | $H_2O_2$ + VII th group element (2) | 732.071 |
| | | I st group + VI th group element (1) | 732.160 |
| | | IV th " + VIII th " " (1) | 732.480 |
| | | V th " + $O_2$ " " (1) | 732.500 |
| | | V th " + I st " " (2) | 732.510 |
| | | V th " + II nd " " (2) | 732.520 |
| | | V th " + V th " " (1) | 732.550 |
| | | V th " + VI th " " (1) | 732.560 |

## SUBJECT INDEX *(continued)*


| | | Title of Table (number of pages) | Table number |
|---|---|---|---|
| 730 | **OXIDATION-REDUCTION,** *(continued)* | | |
| | **Compounds (ions) of different elements** | | |
| | | V th group + VII th group element (6) | 732.570 |
| | | V th " + VIII th " " (1) | 732.580 |
| | | VI th " + VI th " " (1) | 732.660 |
| | | VI th " + VII th " " (2) | 732.670 |
| | | VII th " + $H_2O_2$ (5) | 732.701 |
| | | VII th " + $O_3$ (1) | 732.703 |
| | | VII th " + V th group element (1) | 732.750 |
| | | VII th " + VI th " " (2) | 732.760 |
| | | VII th " + VII th " " (2) | 732.770 |
| | | VII th " + VIII th " " (2) | 732.780 |
| | | VIII th " + VI th " " (1) | 732.860 |
| | | VIII th " + VII th " " (2) | 732.870 |
| 740 | **OXIDATION-REDUCTION, Organic + Inorganic compound** | | |
| | | Organic compound + $O_3$ (2) | 742.403 |
| | | Aliphatic " + VI th group element (2) | 742.461 |
| | | Aliphatic compound + VII th group element (5) | 742.471 |

# ALPHABETICAL INDEX

The first two digits indicate the corresponding **Section.** For the *tables* included under the section (designated by numbers beginning with these two digits), consult the Table of Contents.


| | | |
|---|---|---|
| Addition | of functional group | 660 |
| | to multiple bond | 620 |
| | oxidative | 640 |
| | ring - opening | 630 |
| Alcoholysis, see Solvolysis | | |
| Associated molecules | dissociation | 500 |
| Association | molecular | 610 |
| | ring - closing | 680 |
| Atom migration | | 150 |
| Beckmann rearrangement | | 160 |
| Bond saturation | | 620 |
| Bond - unsaturation | decomposition | 520 |
| | elimination | 420 |
| Branching isomerization | | 140 |
| Cis-trans isomerization | | 120 |
| Condensation | ester | 200 |
| | nonester | 230 |
| Coordinative exchange | | 380 |
| Decomposition | bond - unsaturating | 520 |
| | of functional group | 560 |
| | pyrolytic | 570 |
| | reductive | 540 |
| | ring - opening | 580 |
| Dismutation | oxidative - reductive | 710 |
| Dissociation | of associated molecules | 500 |
| | of molecular compounds | 510 |
| Double bond shift | | 150 |
| Elimination | bond - unsaturating | 420 |
| | on fifth - group element | 450 |
| | of functional group | 460 |
| | of proton | 400 |
| | ring - closing | 430 |
| Ester | exchange | 220 |
| | solvolysis | 210 |
| Esterification | | 200 |

## ALPHABETICAL INDEX *(continued)*


| | | |
|---|---|---|
| Exchange | coordinative | 380 |
| | ester | 220 |
| | on fifth - group element | 350 |
| | of hydrogen | 310 |
| | isotopic | 300 |
| | of position | 160 |
| | of substituents | 330 |
| Functional group | addition | 660 |
| | decomposition | 560 |
| | elimination | 460 |
| | exchange | 330 |
| Group migration | | 150 |
| Hydrogen | exchange | 310 |
| | migration | 150 |
| | substitution | 310 |
| Hydrolysis, see Solvolysis | | |
| Isomerization | Beckmann | 160 |
| | branching | 140 |
| | cis - trans | 120 |
| | double bond shift | 150 |
| | migration | 150 |
| | racemization | 110 |
| | ring - closing | 170 |
| | ring - opening | 180 |
| | syn - anti | 130 |
| Isotope exchange | | 300 |
| Migration | atom or group | 150 |
| Molecular association | | 610 |
| Molecular - compound | dissociation | 510 |
| Nonester | condensation | 230 |
| | Solvolysis | 240 |
| Ortho - para conversion | | 100 |
| Oxidation - reduction | dismutation | 710 |
| | of compounds of different elements | 730 |
| | of compounds of the same element | 720 |
| | of organic compounds | 740 |
| Oxidative addition | | 640 |
| Position exchange | | 160 |
| Pyrolysis | | 570 |
| Quaternary base | elimination from | 450 |
| | formation | 650 |

## ALPHABETICAL INDEX *(continued)*


Racemization . . . . . 110

Rearrangement, see Isomerization

Reduction, see Oxidation - reduction

Reductive decomposition . . . . . 540

Ring - closing association . . . . . 680
decomposition . . . . . 580
isomerization . . . . . 170

Ring - opening addition . . . . . 630
decomposition . . . . . 580
isomerization . . . . . 180

Saturation, see Bond saturation

Shift of double bond . . . . . 150

Solvolysis, ester . . . . . 210
on fifth - group element . . . . . 250
nonester . . . . . 240

Substituent exchange . . . . . 330

Substitution of hydrogen . . . . . 310

Syn - anti isomerization . . . . . 130

Unsaturation, see Bond unsaturation

# LITERATURE REFERENCES

## Code abbreviations for the most frequently quoted Periodicals

| Abbreviation | Title |
|---|---|
| *ACJ* | Amer. Chem. Journal |
| *ACS* | J. Amer. Chem. Soc. |
| *APU* | Acta physicochim. USSR |
| *BCB* | Bull. Soc. chim. Belg. |
| *BCF* | Bull. Soc. chim. France |
| *BDC* | Ber. Deutche Chem. Ges. |
| *CIL* | J. Soc. Chem. Ind. London |
| *CJR* | Canadian J. Res. |
| *CRA* | Compt. rend. Acad. Sci. Paris |
| *CRV* | Chem. Reviews |
| *CSL* | J. Chem. Soc. London |
| *DAN* | Doklady Akad. Nauk SSSR |
| *GCI* | Gazz. chim. Ital. |
| *HCA* | Helv. chim. Acta |
| *HPA* | Helv. phys. Acta |
| *IEC* | Indust. Engin. Chem. |
| *JCC* | J. chim. phys. et coll. |
| *JCP* | J. Chem. Phys. |
| *JOC* | J. Org. Chem. |
| *JPC* | J. Phys. Chem. |
| *JPR* | J. Phys. Radium |
| *JPS* | J. Polymer. Sci. |
| *MHC* | Monatshefte f. Chemie |
| *PRS* | Proc. Roy. Soc. |
| *RTC* | Rec. trav. chim. Pays Bas |
| *TFS* | Trans. Faraday Soc. |
| *ZAC* | Zeitschr. anorg. allg. Chem. |
| *ZEC* | Zeitschr. f. Elektrochem. |
| *ZPC* | Zeitschr. f. physik. Chem. |
| *ZhFKh* | Zhur. fizicheskoi Khim. |
| *ZhOKh* | Zhur. obshchei Khim. |
| *ZhPKh* | Zhur. priklad. Khim. |

# TABLES OF NUMERICAL DATA

# of

# HOMOGENEOUS CHEMICAL REACTION KINETICS

## INTRODUCTION

The purpose of these Tables is a critically evaluated compilation of the available *factual* numerical data on rates and rate constants of homogeneous chemical reactions. Stress was laid throughout on experimentally ascertained facts; data largely contingent on interpretations have generally not been included.

**Reaction equations** are written in the simplest possible way, on the sole basis of the *observed* overall chemical change. The products are specified for each reaction, unless all reactions of a table are of a common type; in that case, the *Reaction Type* is stated once and for all at the head of the table, and the products, being unequivocally obvious from the type of the reaction, are not repeated. Whenever a reaction gives rise to a variety of products in no simple stoichiometric relation to the reactants, as is the case especially in many gaseous reactions, the products are separated by commas.

**Symbols for Reactants and Products.** By convention, and for the purpose of formulation of the rate laws, reactants and products are designated by Roman-type capital letters $A + B + C.... \rightarrow L + M + N....$, in the order in which they are written down in the reaction equation. As an example, in the reaction written $CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$, A stands for $CH_3COOC_2H_5$, B for $OH^-$, L for $CH_3COO^-$, M for $C_2H_5OH$.

**Units of amount.** The unit of "amount" (concentration, pressure), in which the rates and rate constants are expressed, unless expressly given for each individual reaction, is stated at the head of each table. Generally, that unit is the concentration unit M/l (moles per liter); data originally expressed in other units have been mostly converted to

M/l. It is known, of course, that for first-order rate constants the unit of concentration is immaterial, if rate and mass-action are in the same unit.

**Units of time and rate.** Throughout these tables, *the unit of time is the second,* and rates are understood to be expressed in the stated "unit of amount" (mostly M/l) *per second.* Original data using units of time other than the second have been systematically converted to seconds. The greatest possible care was exercised to gain complete certainty about the time and rate units involved in the original data. Authors are all too often neglectfully reticent or even confusing on that point, and the process of ascertaining the units has often been laborious.

**Base of logarithms.** The integrated forms of the rate laws generally involve natural logarithms, and the correct value of the rate constant $k$ is that calculated from the integrated equation with *natural logarithms.* Practically, numerical calculations are mostly made with the use of decimal logarithms, which amounts to a division of the true $k$ by ln 10, and necessitates remultiplication by that factor. In all too many instances, this simple operation is either omitted, or, worse yet, there is no hint or clue as to whether it has or has not been carried out, with a resulting uncertainty in $k$ by a factor of 2.303. It has been our strenuous endeavor to make sure, in each doubtful case, often at the cost of laborious search, of the kind of logarithm actually meant in the original. All $k$ in these Tables are the *true* $k$, i.e. based on natural logarithms. The necessary conversions have been made wherever they were called for.

**Uniformity of units.** These recalculations have resulted in a tabulation of data in uniform units throughout these Tables, rates per second, rate constants calculated with natural logarithms. In many instances, rate constants, not included in the original publication, have been calculated in these units, from the experimental data material; the gain, in terms of ready comparison of data from different sources, and of intercommunication, is obvious.

**Rate measured.** The expression "rate of the reaction" is not necessarily unambiguous. It *may* make a difference whether the "rate" meant is that of the disappearance of a reactant or of the formation of a product, and it often does make a difference *which* reactant or *which*

product is meant. There are instances where authors speak loosely of a "rate of the reaction" where a precision about the exact rate referred to would be essential. It has been our endeavor, throughout these Tables, to leave no doubt on that point, and to state the exact nature of the change referred to by the "rate" wherever there might be an ambiguity. In particular, in gaseous reactions giving rise to a variety of products, it is always essential to state whether the rate is that of the disappearance of a given reactant, of the formation of a product (and of which), or, as is often the case, merely of a change of pressure which often stands in no known relation to the rate of formation of a definite product. Similarly, in the case of a reactant undergoing parallel transformations in different directions, it is essential to state whether the rate refers to the total consumption of the reactant or to one or two specific reactions. The necessary statements are given either for separate reactions or, whenever they apply to a whole group of reactions of common type, at the head of the table. They are omitted wherever there can be no ambiguity.

**Defined mass-action law.** Empirical rate laws are tabulated in their differential form, the left-hand member of the equation (written down only if necessary to avoid ambiguity) being understood to be the momentary *rate* measured, in the stated unit of amount per second, and the right-hand member the mass-action law in the form of an algebraic function $k\,f(A, B, \ldots L, M, \ldots X)$ where A, B... are the momentary amounts of the reactants, L, M.... those of the products, X the amount of a catalytically active homogeneous catalyst or inhibitor, if any. Integrated rate equations, being merely a matter of mathematical technique, are not tabulated. Wherever necessary, the differential rate law was reconstituted from the integrated equation.

The "defined mass-action law" is given *primarily as a definition of the rate constants* $k$ the values of which are listed in the tables. It is not necessarily, and often quite certainly is not, the "rate law" of the reaction. It could be a matter of choice; the rate of an actually overall second-order reaction, first-order in reactant A, and first-order in reactant B, normally to be represented by a mass-action function $k\,AB$, can be described by

a first-order function $k'$ A on the understanding that [B] is included in $k'$ which, of course, will then vary with [B], unless, as is often the case, [B] is kept constant throughout the investigation. If the rate constant of a reaction between A and B is defined by a first-order mass-action function $k'$ A, it means, generally, that the order of the mass-action of B is left open. In instances where the experimental material warranted it, we have often derived a more explicit "defined mass-action law" than that used by the original author, and recalculated $k$ accordingly. In all cases, however, greatest care was taken to establish a clearcut correspondence between the *definition* of the $k$ by the "defined mass-action law" and its tabulated numerical values. Unless otherwise stated, the defined $k$ is understood to be constant over the reaction, and to reflect its order under the given conditions.

**Temperature.** All temperatures are in degrees Celsius (centigrade). Temperatures originally expressed on other scales have been converted to °C.

**Rate constants** as defined under "defined mass-action law", are given in the form $k = k^{o} \times 10^{n}$, with the values of $k^{o}$ and $n$ tabulated in adjacent columns, opposite the temperature to which they refer. The symbol $k^{o}$ is the value of $k$ in the order-of-magnitude unit $10^{n}$, and must not be confused with any standard-state value.

**Activation energies** $E$, always in kcal/mole, are given with one digit at most after the decimal point.

**Frequency factors** $A$, defined by the Arrhenius equation $k = Ae^{-E/RT}$, are given in the same form as $k$, namely $A = A^{o} \times 10^{n}$, with $A^{o}$ and $n$ tabulated in adjacent columns. $A$ is of the same dimension and in the same units as $k$.

**Activation heats,** $\Delta H_a$ (kcal/mole), and **Activation entropies,** $\Delta S_a$ (cal/mole/degree °C), are given occasionally under these headings.

**Empirical rates,** in the stated units of amount per second, especially initial rates under fixed conditions, are reproduced occasionally as possibly useful factual numerical data where no mass-action law and no rate constant defined by a mass-action law can be derived from

the available data.

By the same token, **Fractional times**, i.e. the time in seconds necessary for the completion of the stated fraction of the full conversion, have been tabulated occasionally, as empirical numerical material. The fraction of completion is stated in bold-face type, in parentheses. However, in all instances where a rate law could be inferred from the data, rate constants $k$, defined by that mass-action law, have been calculated and tabulated in preference to fractional times.

**Initial concentrations.** The range of amounts of reactants and products in which the rates and rate constants have been established is extremely important. A rate law may hold in one range but be utterly invalid in a different range. A statement of the initial range is included, under the heading "Amount of reactant," wherever that information is available. Reactants and products are referred to, as usual, by A, B..., L, M... . It is immediately obvious that the merits of the "defined mass-action law" and the strength of its claim to the dignity of a rate law, are largely dependent on the breadth of the concentration range in which the mass-action law was found to hold. It will be noted that not infrequently rates and rate constants have been determined only for one definite composition of the reactant mixture. Listing of data of $k$ implies, of course, that $k$ is satisfactorily constant throughout the reaction (except as qualified in the Comments), i.e. the given mass-action law renders the order of the reaction with the stated initial amounts.

**Addend (Catalyst).** Addends, other than the explicit participants A, B...., L, M...., are listed under that heading, with their amounts or ranges of amounts in the adjacent column. If the addend has a catalytic effect, its concentration is either implicitly contained in $k$, or explicitly in the mass-action function. The "defined mass-action law" is always so formulated that there can be no doubt on that point.

**Solvent (Medium).** In the case of liquid-phase reactions in solution, the solvent is stated in the column immediately following the Reaction equation. If the "solvent" is identical

with one of the reactants, it is designated by the corresponding Capital-letter symbol. Composite solvents are frequently *coded*, e.g. Et 85 for $C_2H_5OH$ 85 vol % + $H_2O$ 15 %; explanation of the code designations will be found at the end of the table.

**Agreeing and conflicting data.** Reduction of the reaction equations to their simplest empirical form, expression of the mass-action functions in the most plausible form, and uniform expression of the rate constants $k$ in standard units, have necessitated and permitted frequent cross-checks and comparisons of data from different sources. Very closely agreeing data have been averaged and are underlined in the Tables. Less closely concordant data, pertaining to overlapping conditions, unless there were reasonable grounds for a selection, have often been left side by side, the range of the variation being useful as a yardstick of the reproducibility of the rate of the reaction. Good agreement of data identically defined but determined in different ranges, adds greatly to the validity of the mass-action function as a true rate law. In the rarer instances of outright irreconcilable conflict, a motivated choice could mostly be made of the more reliable data; the editors do not, however, claim to be infallible, and will be receptive of criticisms. The degree of agreement or conflict of data from different sources is obvious from the tables, and is furthermore expressly stressed in the Comments placed at the end of the table.

**Rate laws.** The editors have knowingly refrained from committing themselves on the essentially controversial question of the true rate law of a reaction. The evaluation of the validity of a mass-action function as a rate law must be left to the judgment of the users of these Tables. The factual data given in these Tables, in particular the ranges of applicability of the "defined mass-action law", the degree of constancy or variation of $k$, its reproducibility as reflected by the agreement of data from different sources, are important elements in this evaluation. Further elements, such as systematic trends of $k$ with the progress of the reaction i.e. as a function of the extent of the conversion, or the degree of homogeneity or partial heterogeneity of a gas-phase reaction, will be found in the Comments. It will be noted that, for a great number of extensively studied fundamentally important gaseous reactions, only *initial* rates and initial rate constants are available, and that reaction-rate orders inferred from variations of initial conditions, i.e. from one run to another, need not hold over the

course of the reaction in one single run, partly on account of the yet insufficiently explored mixed homogeneous-heterogeneous and nonstationary character of these reactions. On many reactions, the scarcity of available numerical data, and their limitations, often contrasting with the imposing amount of existing brilliant even though maybe premature speculation, will be found disappointing. The Tables cannot, in this field, but tacitly dramatize the scantiness of our present factual knowledge.

**Supplementary tables,** placed after the main table, give additional useful numerical information which could not be fitted into the pattern of the table. The selection of topics was, of necessity, arbitrary. Secondary effects, in particular the great variety of salt effects, etc., especially if investigated for purposes outside the field of Kinetics, could not be included, but references thereto are generally given.

**Comments** at the end of the table cover, in a terse style, a variety of additional items of information both on the table as a whole and on particular reactions, including pertinent elements of evaluation. Reactions commented upon are marked in the table with an asterisk *.

**Literature** lists of references used or at least mentioned in Comments are placed at the very end of each table. References are arranged in the alphabetical order of the names of first authors, and are numbered in small type, e.g. ([12]). The sources of the data tabulated in the table are designated by these literature references numbers. Literature references examined but neither used nor mentioned are not included.

**Order within the table.** Reactions are arranged and numbered, without strict adherence to any ironclad system, in the usual order of increasing complexity of the key reactant, thus, in the case of organic compounds, in the order of increasing numbers of C atoms, branched isomers placed after the normal-chain isomers; not developed organic-compound formulas, e.g. $C_5H_{11}OH$, always mean the normal compound. Substituted derivatives are arranged in an order corresponding to that of the periodic system, e.g. alkyl-substituted, nitro-substituted, sulfo-substituted, halogen-substituted; the latter in the order F, Cl, Br, I. Longer tables are often subdivided, and the subdivisions are listed in the Comments of the table.

**Pattern of the tables.** The patterns of columns and headings vary somewhat from one table to another, depending on their contents. Where the width of a column was insufficient, and space was available in adjacent columns, free neighboring space was borrowed and the encroachment clearly marked by horizontal lines enclosing the extraneous parts.

**Errors and omissions** are unavoidable in Tables. The loose-leaf form has been chosen in view of the ease of subsequent revisions of individual sheets, including deletions, replacements, and additions. We shall welcome criticisms and communications pointing out errors and gaps.

**Acknowledgments.** The editor and his associates gratefully acknowledge the interest and help of the National Bureau of Standards, of the Committee on Tables of Constants, National Research Council, of Princeton University, and of the correspondents and authors to whom we have had many an occasion to turn for advice.

Editor

# Tables of Chemical Kinetics

## Homogeneous Reactions

# ORTHO - PARA CONVERSION

*Gas phase*

**Homogeneous Reactions**

**101.000.**

Rates are in "unit of amount" per sec.

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $o\text{-}H_2 \rightleftharpoons p\text{-}H_2$ | thc | mm Hg | 50 - 400 | | | $k\,(A - A_e)\,(A + L)^{1/2}$ | 600 | 3.3 | -5 | | * | (1) (11) (7) |
| | | | | | | | | 700 | 1.1 | -3 | 58 | | |
| .2 | $o\text{-}H_2 \rightarrow p\text{-}H_2$ | from (.1) | " | " | | | $k_1\,A(A + L)^{1/2}$ | 600 | 8.0 | -6 | | | " |
| | | | | | | | | 700 | 2.7 | -4 | 58 | | |
| .3 | $p\text{-}H_2 \rightarrow o\text{-}H_2$ | from (.1) | " | " | | | $k_2\,A(A + L)^{1/2}$ | 600 | 2.5 | -5 | | | |
| | | | | | | | | 700 | 8.0 | -4 | 58 | | " |
| .4 | $o\text{-}H_2 \rightleftharpoons p\text{-}H_2$ | thc | M/l | 10 - 500 mm Hg | X = | | $k\,(A - A_e)X$ | | | | | * | (10) |
| | | | | | | 1 - 170 mm Hg | | | | | | | (8) |
| | | | | | $O_2$ | | | -80 | 1.2 | -1 | | | (3) |
| | | | | | | | | ~ 20 | 1.5 | -1 | | | (13) |
| | | | | | | | | 100 | 1.7 | -1 | | | (9) |
| | | | | | | | | | | | | | (6) |
| | | | | | | | | | | | | | (12) |
| | | | | | NO* | " | " | -80 | 6.0 | -1 | | | |
| | | | | | | | | ~ 20 | 6.0 | -1 | | | |
| | | | | | $NO_2$ | " | " | ~ 20 | 2.1 | -1 | | | |
| | | | | | | | | 100 | 2.3 | -1 | | | |
| | | | | | I | | " | 420 | 2.6 | 0 | | | |
| | | | | | | | | 480 | 1.0 | +1 | | | |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $o\text{-}H_2 \rightleftarrows p\text{-}H_2$ *(continued)* | thc | M/l | 10 - 500 mm Hg | $B_2H_6$ | | $k\ (A - A_e)X$ | ~ 20 | 1.8 | -4 | | | |
| | | | | | | | | 100 | 1.4 | -1 | | | |
| .5 | $o\text{-}H_2 \rightarrow p\text{-}H_2$ | from (.4) | M/l | 10 - 500 mm Hg | X = | | $k_1$ AX | | | | | * | |
| | | | | | $O_2$ | 1 - 170 mm Hg | | -80 | 3.0 | -2 | | | |
| | | | | | | | | ~ 20 | 3.7 | -2 | | | |
| | | | | | | | | 100 | 4.2 | -2 | | | |
| | | | | " | NO* | " | | -80 | 1.5 | -1 | | | |
| | | | | | | | | ~ 20 | 1.5 | -1 | | | |
| | | | | " | $NO_2$ | " | | ~ 20 | 5.2 | -2 | | | |
| | | | | | | | | 100 | 5.5 | -2 | | | |
| | | | | " | I | | | 420 | 6.5 | -1 | | | |
| | | | | | | | | 480 | 2.5 | 0 | | | |
| | | | | " | $B_2H_6$ | | | ~ 20 | 6.7 | -5 | | | |
| | | | | | | | | 100 | 3.5 | -2 | | | |
| .6 | $p\text{-}H_2 \rightarrow o\text{-}H_2$ | from (.4) | M/l | 10 - 500 mm Hg | X = | | $k_2$ AX | | | | | * | |
| | | | | | $O_2$ | 1 - 170 mm Hg | | -80 | 9.0 | -2 | | | |
| | | | | | | | | ~ 20 | 1.1 | -1 | | | |
| | | | | | | | | 100 | 1.3 | -1 | | | |
| | | | | " | NO* | " | | -80 | 4.5 | -1 | | | |
| | | | | | | | | ~ 20 | 4.5 | -1 | | | |
| | | | | " | $NO_2$ | " | | ~ 20 | 1.6 | -1 | | | |
| | | | | | | | | 100 | 1.8 | -1 | | | |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $p\text{-}H_2 \rightarrow o\text{-}H_2$ *(continued)* | from (.4) | M/l | 10 - 500 mm Hg | I | | $k_2$ AX | 420 | 1.9 | 0 | | | |
| | | | | | | | | 480 | 7.5 | 0 | | | |
| .7 | $o\text{-}D_2 \rightleftharpoons p\text{-}D_2$ | thc | mm Hg | 10 | | | $k\ (A - A_e)(A + L)^{1/2}$ | 660 | 1.4 | -4 | | * | (2) |
| | | | | | | | | 700 | 4.3 | -4 | | | |
| .8 | $o\text{-}D_2 \rightarrow p\text{-}D_2$ | from (.7) | mm Hg | 10 | | | $k_1\ A(A + L)^{1/2}$ | 660 | 4.6 | -5 | | | |
| | | | | | | | | 700 | 1.4 | -4 | | | |
| .9 | $p\text{-}D_2 \rightarrow o\text{-}D_2$ | from (.7) | mm Hg | 10 | | | $k_2\ A(A + L)^{1/2}$ | 660 | 9.2 | -5 | | | |
| | | | | | | | | 700 | 2.9 | -4 | | | |
| .10 | $o\text{-}D_2 \rightleftharpoons p\text{-}D_2$ | thc | M/l | | X = | | $k\ (A - A_e)X$ | | | | | * | (5) (3) |
| | | | | | $O_2$ | | | -80 | 1.2 | -2 | | | (4) |
| | | | | | | | | 20 | 1.4 | -2 | | | |
| | | | | | NO* | | | -80 | 6.0 | -2 | | | |
| | | | | | | | | 20 | 6.0 | -2 | | | |
| .11 | $o\text{-}D_2 \rightarrow p\text{-}D_2$ | from (.10) | M/l | | $O_2$ | | $k_1$ AX | -80 | 3.8 | -3 | | | |
| | | | | | | | | 20 | 4.7 | -3 | | | |
| | | | | | NO* | | " | -80 | 2.0 | -2 | | | |
| | | | | | | | | 20 | 2.0 | -2 | | | |
| .12 | $p\text{-}D_2 \rightarrow o\text{-}D_2$ | from (.10) | M/l | | $O_2$ | | $k_2$ AX | -80 | 7.7 | -3 | | * | |
| | | | | | | | | 20 | 9.4 | -3 | | | |
| | | | | | NO* | | " | -80 | 4.0 | -2 | | | |
| | | | | | | | | 20 | 4.0 | -2 | | | |

## COMMENTS

(.1) (.4) (.7) (.10) The kinetics of the conversion in both directions are represented by a single rate law with a single rate constant $k = k_1 + k_2$, with $k_1$ pertaining to the ortho → para, $k_2$ to the para → ortho conversion; the acting mass is the distance $(A - A_e)$ of the concentration of the reactant A from its equilibrium concentration $A_e$. The separate ortho → para rate constants $k_1$ (.2) (.5) (.8) (.11) and the para → ortho rate constants $k_2$ (.3) (.6) (.9) (.12) are derived from the corresponding ortho ⇄ para $k$ and the equilibria. The equilibria give, at ∞ temperature (and with sufficient accuracy at the temperatures listed), for $o\text{-}H_2 \rightleftarrows p\text{-}H_2$, $k_1 = k/4$ and $k_2 = 3k/4$ and for $o\text{-}D_2 \rightleftarrows p\text{-}D_2$, $k_1 = k/3$ and $k_2 = 2k/3$. The experimentally feasible $(A - A_e)$ are positive with respect to $p\text{-}H_2$ and to $o\text{-}D_2$ at the temperatures listed.

*Uncatalyzed reactions* (.1) (.2) (.3) (.7) (.8) (.9): the form of the rate laws is accounted for by the catalytic action of H (D) atoms, exemplified by $o\text{-}H_2 + H \rightarrow H + p\text{-}H_2$.

*Catalyzed reactions* (.4) (.5) (.6) (.10) (.11) (.12): $NO^*$ is the paramagnetic first excited state (353 cal); $k$ at 20° calculated at total NO = 12 mm Hg. Iodine-catalyzed reaction calculated from conversion in $H_2 + I_2$, subtracting that due to atomic H. Catalysis by $O_2$, $NO^*$, $NO_2$, I, is attributed to magnetic moment; catalysis by $B_2H_6$ to exchange of H between $B_2H_6$ and $H_2$.

## LITERATURE

(1) A. Farkas, *ZPC*[B] 1930, **10**, 419. (2) A. Farkas, L. Farkas, *PRS*[A] 1935, **152**, 124. (3) A. Farkas, L. Farkas, *PRS*[A] 1935, **152**, 152. (4) A. Farkas, L. Farkas, P. Harteck, *PRS*[A] 1934, **144**, 481. (5) A. Farkas, U. Garbatski, *JCP* 1938, **6**, 260. (6) L. Farkas, U. Garbatski, *JCP* 1938, **6**, 260. (7) L. Farkas, P. Harteck, *ZPC*[B] 1934, **25**, 257. (8) L. Farkas, H. Sachsse, *ZPC*[B] 1933, **23**, 1. (9) L. Farkas, H. Sachsse, *TSF* 1934, **30**, 331. (10) L. Farkas, H. Sachsse, *Sitzber. Preuss. Akad. Wiss.* 1933, 268.

(11) K. H. Geib, P. Harteck, *ZPC* 1931, *Bodensteinband*, 849. (12) E. J. Rosenbaum, T. R. Hogness, *JCP* 1934, **2**, 267. (13) H. Sachsse, *ZEC* 1934, **40**, 531.

# ORTHO-PARA CONVERSION

*Liquid phase*

**Homogeneous Reactions**
**102.000.**

Rates are in "unit of amount" per sec.

| No. | Reaction | Medium (solvent) | Method | Unit of amount | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $o-H_2 \rightarrow p-H_2$ | pure | thc | M % | 75 | | | $kA^2$ | ~ 25 | 3.3 | -8 | ~ 0 | | (3) (4) (9) (1) |
| .2 | $o-H_2 \rightleftarrows p-H_2$ | $S = H_2O$ | thc | M/l | sat, | | | $k(A - A_e)S$ | ~ 20 | 1.1 | -6 | | | (8) (5) (6) |
| | | $D_2O$ | | | 1 atm | | | | | 4.8 | -7 | | * | |
| | | $C_6H_6$ | | | | | | | | 2.8 | -6 | | | |
| | | $CS_2$ | | | | | | | | 3.8 | -7 | | | |
| | | $CCl_4$ | | | | | | | | 4.5 | -7 | | | |
| | | $C_6H_5NH_2$ | | | | | | | | 3.9 | -6 | | | |
| | | $CH_3OH$ | | | | | | | | 2.0 | -6 | | | |
| | | $C_6H_{11}OH$ | | | | | | | | 2.7 | -6 | | | |
| .3 | $o-H_2 \rightarrow p-H_2$ | $S = H_2O$ | from .2 | M/l | sat, | | | $k_1AS$ | ~ 20 | 2.8 | -7 | | | (8) (5) (6) |
| | | $D_2O$ | | | 1 atm | | | | | 1.2 | -7 | | * | |
| | | $C_6H_6$ | | | | | | | | 7.2 | -7 | | | |
| | | $CS_2$ | | | | | | | | 1.0 | -7 | | | |
| | | $CCl_4$ | | | | | | | | 1.2 | -7 | | | |
| | | $C_6H_5NH_2$ | | | | | | | | 9.7 | -7 | | | |
| | | $CH_3OH$ | | | | | | | | 5.2 | -7 | | | |
| | | $C_6H_{11}OH$ | | | | | | | | 6.8 | -7 | | | |

| No. | Reaction | Medium (solvent) | Method | Unit of amount | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $p - H_2 \rightarrow o - H_2$ | S = $H_2O$ | from .2 | M/l | sat, | | | $k_2AS$ | ~ 20 | 8.5 | -7 | | | (6) (5) (6) |
| | | $D_2O$ | | | 1 atm | | | | | 3.7 | -7 | | * | |
| | | $C_6H_6$ | | | | | | | | 2.1 | -6 | | | |
| | | $CS_2$ | | | | | | | | 2.8 | -7 | | | |
| | | $CCl_4$ | | | | | | | | 3.3 | -7 | | | |
| | | $C_6H_5NH_2$ | | | | | | | | 2.9 | -6 | | | |
| | | $CH_3OH$ | | | | | | | | 1.5 | -6 | | | |
| | | $C_6H_{11}OH$ | | | | | | | | 2.0 | -6 | | | |
| .5 | $o - H_2 \rightleftarrows p - H_2$ | $H_2O$ | thc | M/l | sat, | X = | | $k(A - A_e)X$ | ~ 20 | | | | | (7) (11) (10) (2) (5) |
| | | | | | 1 atm | $PrCl_3$ | 0.0025 - 0.020 | | | 3.8 | -2 | | * | |
| | | | | | | $NdCl_3$ | | | | 4.0 | -2 | | | |
| | | | | | | $SmCl_3$ | | | | 1.1 | -2 | | | |
| | | | | | | $GdCl_3$ | | | | 2.9 | -1 | | | |
| | | | | | | $ErCl_3$ | | | | 6.4 | -1 | | | |
| | | | | | | $YbCl_3$ | | | | 1.7 | -1 | | | |
| | | | | | | $CuCl_2$ | | | | 2.0 | -2 | | | |
| | | | | | | $NiSO_4$ | | | | 3.5 | -2 | | | |
| | | | | | | $CoSO_4$ | 0.001 - 1.0 | | | 9.3 | -2 | | | |
| | | | | | | $FeSO_4$ | | | | 1.0 | -1 | | | |
| | | | | | | $MnSO_4$ | | | | 1.4 | -1 | | | |
| | | | | | | $Fe_2(SO_4)_3$ | | | | 8.3 | -2 | | | |
| | | | | | | $Cr_2(SO_4)_3$ | | | | 3.7 | -2 | | | |

| No. | Reaction | Medium (solvent) | Method | Unit of amount | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $o - H_2 \rightleftarrows p - H_2$ *(continued)* | $H_2O$ | thc | M/l | sat, 1 atm | $O_2$ | | $k(A - A_e)X$ | ~ 20 | 1.8 | -1 | | | |
| | | | | | | NO | | | | 4.4 | -1 | | | |
| | | $C_2H_5OH$ | " | " | " | $NiSO_4$ | 0.001 | " | " | 3.3 | -2 | | | |
| | | | | | | $FeSO_4$ | " | | | 1.0 | -1 | | | |
| | | | | | | $MnSO_4$ | " | | | 9.8 | -2 | | | |
| | | | | | | $Fe_2(SO_4)_3$ | " | | | 8.0 | -2 | | | |
| .6 | $o - D_2 \rightleftarrows p - D_2$ | $S = H_2O$ | thc | M/l | sat, 1 atm | | | $k(A - A_e)S$ | ~ 20 | 6.0 | -7 | | * | ([8]) |
| | | $C_6H_6$ | | | | | | | | 7.0 | -7 | | | |
| | | $CS_2$ | | | | | | | | 8.5 | -8 | | | |
| | | $CCl_4$ | | | | | | | | 8.5 | -8 | | | |
| .7 | $o - D_2 \rightarrow p - D_2$ | $S = H_2O$ | from .6 | M/l | sat, 1 atm | | | $k_1AS$ | ~ 20 | 1.4 | -7 | | * | ([8]) |
| | | $C_6H_6$ | | | | | | | | 2.3 | -7 | | | |
| | | $CS_2$ | | | | | | | | 2.8 | -8 | | | |
| | | $CCl_4$ | | | | | | | | 2.8 | -8 | | | |
| .8 | $p - D_2 \rightarrow o - D_2$ | $S = H_2O$ | from .6 | M/l | sat, 1 atm | | | $k_2AS$ | ~ 20 | 2.8 | -7 | | * | ([8]) |
| | | $C_6H_6$ | | | | | | | | 4.7 | -7 | | | |
| | | $CS_2$ | | | | | | | | 5.7 | -7 | | | |
| | | $CCl_4$ | | | | | | | | 5.7 | -7 | | | |



942151 O—51——3

## COMMENTS

(.2) (.3) (.4) $k = k_1 + k_2$; $k_2/k_1 = 3$. The formulation (.2) is valid for the reaction in either direction, in terms of the mass action of the distance from equilibrium $(A - A_e)$. (.5) $k = k_1 + k_2$; the formulation of the rate law is analogous to that under (.2), in terms of the distance from equilibrium; the ratio $k_2/k_1$ remains = 3. (.6) (.7) (.8) Formulation (.6) analogous to that of (.2), in terms of distance from equilibrium $(A - A_e)$; $k = k_1 + k_2$; $k_2/k_1 = 2$.

## LITERATURE

(1) K. F. Bonhoeffer, P. Harteck, *Sitzber. Preuss. Akad. Wiss.* 1929, 103. (2) M. Calvin, *ACS* 1938, 60, 2003. (3) E. Cremer, *ZPC*$^B$ 1935, 28, 199. (4) E. Cremer, M. Polanyi, *ZPC*$^B$ 1933, 21, 459. (5) L. Farkas, H. Garbatski, *TSF* 1939, 35, 263. (6) L. Farkas, H. Sachsse, *ZPC*$^B$ 1933, 23, 1. (7) L. Farkas, H. Sachsse, *ZPC*$^B$ 1933, 23, 19. (8) L. Farkas, L. Sandler, *TSF* 1939, 35, 337. (9) W. H. Keesom, J. de Smedt, H. H. Mooy, *Proc. Konink. Akad. Wet. Amsterdam*, 1930, 33, 814. (10) H. Sachsse, *ZEC* 1934, 40, 531.

(11) H. Sachsse, *ZPC*$^B$ 1934, 24, 429.

# ORTHO-PARA CONVERSION



Amounts are in mole %.
Rates in mole % per sec.

| No. | Reaction | Method | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | |
| .1 | $o - H_2 \rightarrow p - H_2$ | thc | 25 - 70 | $kA^2$ | ~ - 263 | 5.4 | -8 | ~ 0 |

## COMMENTS

The rate constant $k$ falls with the progress of the reaction as the molecules become increasingly separated in the lattice. With an initial $A_o$ = 75 mole %, $k$ begins to fall off at A = 25 %. The reaction comes to a halt at A = 19 %.

## LITERATURE

E. Cremer, *ZPC*[B] 1935, **28**, 199
E. Cremer, M. Polanyi, *ZPC*[B], **21**, 459

# RACEMIZATION

## Organic halogen compounds

*Gas phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Active compound | Unit of amount | Amount of reactant | Addend (Catalyst) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | d-$C_2H_5CH(CH_3)I$ | M/l | 100 - 200 | $I_2$ | $kA(I_2)^{-1/2}$ | 238.0 | 3.53 | -2 | | ([1]) |
| | | | | | | 255.5 | 1.01 | -1 | | |
| | | | | | | 276.0 | 3.14 | -1 | 32.2 | |

## COMMENTS

Catalyzed by $I_2$ formed through decomposition of A. The mechanism is: $I_2 \rightleftharpoons I + I(K)$; $I + d - A \xrightarrow{1} l - A + I$; $k = 2k_1K^{1/2}$. See the decomposition reaction $2A \rightarrow C_4H_{10} + C_4H_{10} + I_2$, 521.477.
Converted from M/ml to M/l.

## LITERATURE

R.A.Ogg, Jr., M.Polanyi, *TFS* 1935, **31**, 482.

# RACEMIZATION

## C, H, O compounds

*Liquid phase*

**Homogeneous Reactions**
**112.440**

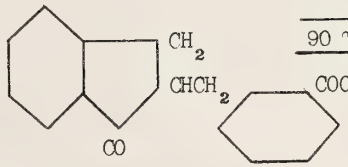
Method: polarimetry

All rates are in "unit of amount" per sec.

| No. | Initial active compound | Solvent (Medium) | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | (+) $C_2H_5CH(CH_3)CHO$ | $H_2O$ + dioxane, *N* | M/l | | $H^+$ | 0.06 – 0.6 | $kA[H^+]$ | | | | | | ([1]) |
| | | 0.274 | | | | | | 25 | | 4.65 | -5 | | |
| | | " | | | | | | 35 | | 1.02 | -4 | | |
| | [see Supplementary Table] | 0.500 | | | | | | 25 | | 1.60 | -4 | | |
| | | " | | | | | | 35 | | 5.09 | -4 | | |
| | | 0.649 | | | | | | 25 | | 2.69 | -4 | | |
| | | " | | | | | | 35 | | 1.33 | -3 | | |
| | | 0.960 | | | | | | 25 | | 3.90 | -3 | | |
| | | " | | | | | | 35 | | 4.60 | -3 | | |
| .2 | l - trans - $COOHCH(CH_3)CH{:}C(CH_3)COOH$ | $H_2O$ | M/l | | | | $kA$ | | (0.5) | | | | ([8]) |
| | COOH | | | | HCl | 0 | | 100 | $6.42 \times 10^4$ | 1.07 | -5 | | |
| | | | | | | 2 | | 100.5 | $7.68 \times 10^4$ | 1.04 | -5 | | |
| | | | | | | 5 | | 101 | $1.95 \times 10^4$ | 3.55 | -5 | | |
| | | | " | | NaOH | 1 | | 101.5 | $1.47 \times 10^3$ | 4.73 | -4 | | |
| | | $(CH_3)_2CO$ | | | – | | | 56.5 | $2.88 \times 10^5$ | 2.44 | -6 | | |
| .3 | d - $CH_3COCH(CH_3)C_2H_5$ | $CH_3COOH$ | M/l | 0.9 | $HNO_3$ | 1.19 | $kA$ | 25.0 | | 4.13 | -3 | | ([2]) |
| | | | | | | | | 38.7 | | 2.17 | -2 | | |
| .4 | d - $C_2H_5COCH(CH_3)C_2H_5$ | $CH_3COOH$ | M/l | 0.9 | $HNO_3$ | 1.19 | $kA$ | 25.0 | | 1.72 | -3 | | ([2]) |
| | | | | | | | | 38.7 | | 5.66 | -3 | | |

| No. | Initial active compound | Solvent (Medium) | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | Fractional time | $k = k^0 \times 10^n$ $k^0$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | d - cyclo - $C_6H_{11}COCH(CH_3)C_2H_5$ | $CH_3COOH$ | M/l | 0.9 | $HNO_3$ | 1.19 | $kA$ | 25.0 | | 3.05 | -4 | | (2) |
| .6 | d - $C_6H_5COCH(CH_3)C_2H_5$ | $CH_3COOH$ | M/l | 0.9 | $HNO_3$ | 1.19 | $kA$ | 36.7 | | 4.94 | -4 | | (2) |
| .7 | l - $C_6H_5COCH(CH_3)C_2H_5$ | dioxane + $D_2O$ 45.0 | g/100 ml | 7.5 | NaOD | 0.43 | | 35.0 | | | | | (5) |
| | | | | | | | | (0.12) | 3600 | | | | |
| | | | | | | | | (0.41) | 11700 | | | | |
| | | | | | | | | (0.65) | 23400 | | | | |
| .8 | $C_6H_5COCH(CH_3)C_6H_5$ | $C_6H_5Cl$ | M/kg | 0.025 | | $c$ | $(k\,c + k'c^2)A$ | | | | | | |
| | | | | | $CCl_3COOH$ | 0.02 - 0.2 | | 99.4 | $k$ | 1.27 | -4 | * | (4) |
| | | | | | | | | " | $k'$ | 7.42 | -4 | | |
| | | | | | $CHCl_2COOH$ | 0.05 - 0.3 | $(k\,c + k'c^{1/2})A$ | | | | | | |
| | | | | | | | | 99.4 | $k$ | 3.35 | -5 | * | " |
| | | | | | | | | | $k'$ | 1.67 | -6 | | |
| | | | | | $CH_2ClCOOH$ | 0.08 - 0.5 | " | " | $k$ | 1.60 | -6 | * | " |
| | | | | | | | | | $k'$ | 1.47 | -6 | | |
| | | | | | o - $NO_2C_6H_4COOH$ | 0.08 - 0.4 | " | " | $k$ | 3.33 | -6 | * | " |
| | | | | | | | | | $k'$ | 1.75 | -6 | | |
| .9 | $C_6H_5COCH[CH(CH_3)C_2H_5]C_6H_5$ | $C_6H_5OCH_3$ | M/kg | 0.028 | $CHCl_2COOH$ | 0.6 | $kAc$ | 100 | | 1.85 | -6 | * | (4) |
| | | | | | ($c$) | 0.4 | | | | 1.73 | -6 | | |
| | | | | | | 0.2 | | | | 7.67 | -7 | | |
| | | $C_6H_5NO_2$ | " | " | " | 0.6 | " | " | | 3.62 | -6 | | " |
| | | | | | | 0.4 | | | | 4.43 | -6 | | |
| | | | | | | 0.1 | | | | 3.89 | -6 | | |

| No. | Initial active compound | Solvent (Medium) | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .9 | $C_6H_5COCH[CH(CH_3)C_2H_5]C_6H_5$ (*continued*) | $C_6H_5Cl$ | M/kg | 0.028 | $CHCl_2COOH$ (*c*) | 0.6 | *k* Ac | 100 | | 8.60 | -6 | | (4) |
| | | | | | | 0.4 | | | | 8.30 | -6 | | |
| | | | | | | 0.1 | | | | 7.12 | -6 | | |
| | | decalin | " | " | " | 0.6 | " | " | | 2.57 | -5 | | " |
| | | | | | | 0.4 | | | | 2.19 | -5 | | |
| | | | | | | 0.1 | | | | 1.43 | -5 | | |
| .10 | d - $C_6H_5CH_2COCH(CH_3)C_2H_5$ | $CH_3COOH$ | M/l | 0.9 | $HNO_3$ | 1.19 | *k* A | 25.0 | | 1.97 | -4 | * | (2) |
| | | | | | | | | 44.6 | | 1.18 | -3 | | |
| .11 | p - $CH_3C_6H_4CH(C_6H_5)COO^-$ | $H_2O$ + 3 % $D_2O$ | M/l | 0.2 | NaOH | 0.22 | *k* A | 100 | | 6.4 | -6 | * | (7) |
| .12 | p - $CH_3C_6H_4CD(C_6H_5)COO^-$ | $H_2O$ | M/l | 0.2 | NaOH | 0.22 | *k* A | 100 | | 1.4 | -6 | * | (7) |
| .13 | $CH_3CH\langle CH_2CH_2 / CH_2CO \rangle CHCH(CH_3)_2$ (menthone) | $C_6H_5Cl$ | wt % (A) M/kg (*c*) | 6.2 ± 0.2 | | *c* | $(k\,c + k'c^{1/2})$A | | | | | | |
| | | | | | $C_6H_5COOH$ | 0.07 - 0.6 | | 99.4 | *k* | 7.35 | -6 | * | (3) |
| | | | | | | | | | *k'* | 5.50 | -6 | | |
| | | " | | " | m - $ClC_6H_4COOH$ | 0.1 - 0.4 | " | " | *k* | 1.33 | -5 | | " |
| | | | | | | | | | *k'* | 1.13 | -5 | | |
| | | " | | " | $CH_2ClCOOH$ | 0.1 - 0.4 | $(k\,c + k'c^2)$ A | | | | | | |
| | | | | | | | | 99.4 | *k* | 4.78 | -5 | | " |
| | | | | | | | | | *k'* | 2.33 | -8 | | |
| | | " | | " | o - $NO_2C_6H_4COOH$ | 0.1 - 0.3 | " | " | *k* | 1.33 | -4 | | " |
| | | | | | | | | | *k'* | 3.33 | -8 | | |
| | | " | | " | $CHCl_2COOH$ | 0.01 - 0.07 | " | " | *k* | 3.33 | -4 | | " |
| | | | | | | | | | *k'* | 5.83 | -7 | | |

| No. | Initial active compound | Solvent (Medium) | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | | $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .13 | $CH_3CH<^{CH_2CH_2}_{CH_2CO}>CHCH(CH_3)_2$ *(continued)* (menthone) | $C_6H_5Cl$ | | 6.2 ± 0.2 | $CCl_3COOH$ | 0.01 - 0.05 | $(k\,c + k'c^2)A$ | 99.4 | $k$ | 1.23 | -3 | | (3) |
| | | | | | | | | | $k'$ | 5.68 | -6 | | |
| | | " | | " | $C_6H_2(OH)(NO_2)_3$ | 0.1 - 0.25 | " | " | $k$ | 9.68 | -5 | | " |
| | | | | | | | | | $k'$ | 1.03 | -7 | | |
| .14 | d -  (2 - o - carboxybenzylindan - 1 - one) | 90 % $CH_3COOH + H_2O$ | M/l | 0.05 | HBr | 0.142 | $k\,A$ | 25 | | 1.25 | -4 | | (6) |
| | | | | | | 0.245 | | | | 2.57 | -4 | | |
| | | | | | | 0.303 | | | | 3.68 | -4 | | |
| | | | | | | 0.352 | | | | 4.95 | -4 | | |
| .15 | Strychnine hydrogen - L - trans - $\alpha, \gamma$ - dimethylglutaconate | $H_2O$ | | | | | $k\,A$ | 100 | | 1.61 | -4 | | (8) |
| | | $(CH_3)_2CO$ | | | | | " | 56.6 | | 1.25 | -4 | | " |

## SUPPLEMENTARY TABLE

(.1) *Activation functions*

| Dioxane, $N$ (mole fraction) | $\Delta H_a$ | $\Delta S_a$ | Dioxane, $N$ (mole fraction) | $\Delta H_a$ | $\Delta S_a$ |
|---|---|---|---|---|---|
| 0.274 | 16.6 | -22.6 | 0.649 | 26.6 | +14.4 |
| 0.500 | 19.0 | -12.2 | 0.960 | 2.7 | -60.4 |

## COMMENTS

(.8) The $c^{1/2}$ term may arise from equilibrium between monomeric and dimeric forms of the acid. The $c^2$ term may arise from acid acting as proton acceptor. (.9) Only 40 % of the reaction (15 % in $C_6H_5NO_2$) followed.

(.11 - .12) Accompanied by H-D exchange at the same rate. Ionic mechanism. (.13) As (.8) The rate law holds to 60 - 80 % completion. At given $c$, $k = k_o(1 - nA)$.

## LITERATURE

(1) E. J. Badin, E. Pacsu, *ACS* 1945, **67**, 1353. (2) P. D. Bartlett, C. H. Stauffer, *ACS* 1935, **57**, 2580.

(3) R. P. Bell, E. F. Caldin, *CSL* **1938**, 382. (4) R. P. Bell, O. M. Lidwell, J. Wright, *CSL* **1938**, 1861.

(5) S. K. Hsü, C. K. Ingold, C. L. Wilson, *CSL* **1938**, 78. (6) C. K. Ingold, C. L. Wilson, *CSL* **1934**, 773.

(7) D. J. Ives, G. V. Wilks, *CSL* **1938**, 1455. (8) T. H. McCombs, J. Packer, J. F. Thorpe, *CSL* **1931**, 547.

# RACEMIZATION

## Organic halogen compounds

Method: polarimetry

*Liquid phase*

All amounts are in M/l.

All rates in M/l per sec.

| No. | Initial active compound | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | d - $CH_3CHBrCOOH$ | $(CH_3)_2CO$ | 0.3 | $Br^-$ | 0.3 | $kA[Br^-]$ | 22 | 5.23 | -4 | * | (1) |
| .2 | d - $C_7H_{15}CHICH_3$ | $(CH_3)_2CO$ | 0.138 | $I^-$ | 0.160 | $kA[I^-]$ | 30 | 1.30 | -3 | * | (2) |
| .3 | $C_6H_5CHClCH_3$ | $(CH_3)_2CO$ | 0.18 | $HgCl_2$ | 0.15 | $kA$ | 20 | 1.42 | -5 | | (4) |
| | | | | | 0.30 | | " | 4.17 | -5 | | |
| | | | | | 0.60 | | " | 1.67 | -4 | | |
| | | | | | 1.20 | | " | 8.33 | -4 | | |
| .4 | d - $C_6H_5CHBrCH_3$ | $(CH_3)_2CO$ | 0.2 | $Br^-$ | 0.2 | $kA[Br^-]$ | 15.2 | 1.85 | -4 | * | (3) |
| | | | | | | | 30 | 8.00 | -4 | | |
| | | | | | | | 40.5 | 1.94 | -3 | | |

## COMMENTS

(.1) The reverse reaction proceeds with the same $k$. Isotopic substitution of Br (see 302.477.) proceeds practically with the same $k$; consequently, the inversion takes place by way of substitution. (.2) The reverse reaction proceeds with the same rate constant; $k$ calculated from the original $N_1$ = constant sum total of all rates of inversion occurring in the system; $k = N_1 A_0 [I^-]$. By the near equality of the rates of inversion and of isotopic substitution of I (see 302.477.), the inversion takes place by way of the substitution $I^- + A \rightarrow L + I^-$. (.4) As (.2).

## LITERATURE

(1) W. A. Cowdrey, E. D. Hughes, J. P. Newell. C. L. Wilson, *CSL* **1938**, 209. (2) E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley, J. Weiss, *CSL* **1935**, 1525. (3) E. D. Hughes, F. Juliusberger, A. D. Scott, B. Topley, J. Weiss, *CSL* **1936**, 1173. (4) D. R. Read, W. Taylor *CSL* **1940**, 679.

# CIS-TRANS ISOMERIZATION

*Gas phase*

## C, H, O compounds

Amounts are in mm Hg.

Rates are in mm Hg per sec.

| No. | Initial isomer | Method | Amount of reactant | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | cis - $CH_3CH{:}CHCH_3$ ( → trans) | melt | 103 | | $k$ A | 390 | 1.0 | -6 | | | | * | ([3]) |
| | | | " | | | 418 | 1.7 | -6 | ~ 18 | | | | |
| | | | 402 | | | 390 | 3.6 | -6 | | | | | |
| | | | | | | 416 | 6.9 | -6 | | | | | |
| | | | 1440 | | | 390 | 3.8 | -6 | | | | | |
| .2 | cis - $CH_3OCOCH{:}CHCOOCH_3$ ( → trans) | melt | 732 | | $k$ A | 300 | 4.3 | -6 | | | | * | ([4]) ([5]) |
| | | | 2140 | | | " | 7.7 | -6 | | | | | |
| | | | 4060 | | | " | 8.3 | -6 | | | | | |
| | | | ∞ | | | " | 1.3 | -5 | 26.5 (280 - 390°) | 1.3 | 5 | | |
| .3 | cis - $C_6H_5CH{:}CHCOOCH_3$ ( → trans) | melt | 6 - 570 | | $k$ A | 380.5 | 4.53 | -4 | 42 (290 - 390°) | 3.5 | 10 | * | ([2]) |
| .4 | cis - $C_6H_5CH{:}CHC_6H_5$ ( → trans) | melt | 5 - 380 | | $k$ A | 320 | 9.9 | -4 | 43 | 6 | 12 | * | ([1]) |
| .5 | trans - $C_6H_5CH{:}CHC_6H_5$ ( → cis) | anal | | $N_2$ | $k$ A | 214 | 1.16 | -6 | | | | | ([6]) |
| | | | | | | 223 | 2.32 | -6 | | | | | |

## COMMENTS

(.1) Order lower than first with a given initial pressure; approximately $A^2$ with respect to initial pressure. (.2) *E* and *A* valid for pressure extrapolated to $\infty$. First order holds at high pressures. Corrected for partial decomposition of the product. (.3) Reverse reaction negligible. Rate falls off at lower pressures. (.4) Partial decomposition of cis, compensated by a conventional equilibrium constant.

## LITERATURE

(1) G.B.Kistiakowsky, W.R.Smith, *ACS* 1934, **56**, 638.

(2) G.B.Kistiakowsky, W.R.Smith, *ACS* 1935, **57**, 269.

(3) G.B.Kistiakowsky, W.R.Smith, *ACS* 1936, **58**, 766.

(4) G.B.Kistiakowsky, M.Nelles, *ZPC* 1931, Bodenstein Festband 369. (5) M.Nelles, G.B.Kistiakowsky, *ACS* 1932, **54**, 2208. (6) T.W.Taylor, A.R.Murray, *CSL* **1938**, 2078.

# CIS-TRANS ISOMERIZATION

## C, H, N compounds

*Gas phase*

Amounts are in mm Hg.
Rates are in mm Hg per sec.

| No. | Initial isomer (→ final) | Method | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | cis - $C_6H_5CH{:}CHCN$ (→ trans) | refr | >150 | $k$ A | 352 | 4.00 | -5 | 46 | 6 | 11 | * | (1) |
| .2 | trans - $C_6H_5CH{:}CHCN$ (→ cis) | refr | >150 | $k$ A | 352 | 2.89 | -5 | 46 | 4 | 11 | * | (1) |

### COMMENTS

(.1 - .2) First-order homogeneous reaction holds at high pressures and temperatures. Heterogeneous reaction prevails at low pressure and temperature.

### LITERATURE

(1) G.B.Kistiakowsky, W.R.Smith, *ACS* 1936, 58, 2428.



942151 O—51——4

# CIS-TRANS ISOMERIZATION

## Organic halogen compounds

*Gas phase*

Amounts are in mm Hg.
Rates are in mm Hg per sec.

| No. | Initial isomer (→ final) | Method | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | trans - ClCH:CHCl (→ cis) | refr | 200 - 700 | $k$ A | 312.5 | 8.76 | -4 (290 - 335°) | 42 | 5 | 12 | * | (1) |
| .2 | α - $C_6H_5CCl:CHC_6H_5$ (→ β) | anal | | $k$ A | 226<br>246 | 1.01<br>4.46 | -5<br>-5 | 37 | | | | (2) |
| .3 | α - $C_6H_5CCl:CClC_6H_5$ (→ β) | anal | | $k$ A | 196 | 1.6 | -6 | 34 | | | | (2) |

## COMMENTS

(.1) Some heterogeneous conversion and partial decomposition.

## LITERATURE

(1) J.Leslie Jones, R.L.Taylor, *ACS* 1940, **62**, 3480.

(2) T.W.Taylor, A.R.Murray, *CSL* **1938**, 2078.

**Homogeneous Reactions**

**122.440.**

Rates are in "unit of amount" per sec.

| No. | Initial isomer ( → final) | Solvent (Medium) | Unit of amount | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | cis - COOHCH:CHCOOH( → trans) | $H_2O$ | M/l | 0.24 - 0.88 | X = | | $k_1A[X]$; $k_2A^2[X]$ | | | | | * | (3) |
| | | | | | HCl | 1.6 | $k_1$ | 99.9 | 1.82 | -5 | | | |
| | | | | | | " | $k_2$ | " | 2.17 | -5 | | | |
| | | | | | | 2.7 | $k_1$ | 79.8 | 4.98 | -6 | | | |
| | | | | | | " | $k_2$ | " | 5.67 | -6 | | | |
| | | | | | | " | $k_1$ | 99.9 | 3.33 | -5 | | | |
| | | | | | | " | $k_2$ | " | 4.15 | -5 | 24.9 | | |
| | | | | | HBr | 1.6 | $k_1$ | 99.9 | 1.13 | -5 | | | |
| | | | | | | | $k_2$ | " | 1.23 | -5 | | | |
| | | | | | $H_2SO_4$ | 2.7 | $k_1$ | 99.9 | 1.56 | -6 | | | |
| | | | | | | | $k_2$ | " | 1.80 | -6 | | | |
| | | | | | $HClO_4$ | 5.2 | $k_1$ | 99.9 | 6.17 | -7 | | | |
| | | | | | | | $k_2$ | " | 7.17 | -7 | | | |
| | | | | | KCNS | 0.04 - 0.09 | $k_1$ | 79.8 | 2.77 | -4 | | | |
| | | | | | | " | $k_2$ | " | 3.87 | -4 | | | |
| | | | | | | " | $k_1$ | 99.9 | 1.23 | -3 | | | |
| | | | | | | " | $k_2$ | " | 1.62 | -3 | 18.8 | | |
| | | | | | NaBr | 1.8 - 5.3 | $k_1$ | 99.9 | 1.20 | -6 | | | |
| | | | | | | | $k_2$ | " | 1.42 | -6 | | | |

| No. | Initial isomer ( → final) | Solvent (Medium) | Unit of amount | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | cis - $C_6H_5CH{:}CHCOOH$ ( → trans) | $C_6H_6$ | M/ml | $10^5A = 3 - 9$ | $I_2$ | $10^5[I_2] = 0.15 - 2.4$ | $kA[I_2]^{1/2}$ | 99.4 | 1.4 | -3 (100 - 125°) | 24.2 | * | (2) |

## COMMENTS

(.1) In the presence of acids, the second-order $k_2$ is more nearly constant throughout a run than the first-order $k_1$ which falls off, particularly in HCl and HBr. With respect to the mass-action of the catalyst X, the order in acids is actually higher than first; this is attributed to catalysis by both the anion of the acid and the proton. With salts, the order with respect to the catalyst is actually first. The catalyzing proton donation is taken to be contributed by the reactant itself. The reaction is complicated by unavoidable simultaneous addition of the anion to the double bond. The true order with respect to the reactant appears to be, in the presence of acids, first, and in the presence of salts, between 1.5 and 2. The rate determining step is assumed to be represented by

$$A + H_3O^+ + Cl^- \rightarrow \begin{matrix} OH \\ OH \end{matrix} > \overset{H\ H\ O}{\underset{Cl}{C{:}C.C.C.OH}} + H_2O$$

(.2) Conductometric method. The rate of the photochemical reaction in $C_6H_6$ solution (1)(2) at 35°C is governed by the same law, $k'A(I_2)^{1/2}$, with $k'$ proportional to the square root of the incident light intensity.

## LITERATURE

(1) A.Berthoud, C.H.Urech, *JCP* 1937, **27**, 291. (2) R.G.Dickinson and Lotzkar, *ACS* 1937, **59**, 472. (3) R.Nozaki, R.Ogg, *ACS* 1941, **63**, 2583.

# CIS-TRANS ISOMERIZATION

## Organic halogen compounds

**Homogeneous Reactions**
**122.470.**

Rates are in "unit of amount" per sec.

| No. | Initial isomer (→ final) | Solvent (Medium) | Unit of amount | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = k^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | *cis* - ClCH:CHCl (→ *trans*) | pure; $C_4H_6$; $C_6H_{12}$; $C_{10}H_{18}$ | mole fraction | < 0.2 | $I_2$ | 0.001 - 0.015 | $kA[I_2]^{1/2}$ | 150 | 4.5 | -5 (150 - 185°) | 31 | | | * | (3) |
| .2 | *cis* - ICH:CHI (→ *trans*) | $C_{10}H_{18}$ | M/ml | 5 - 10 mole % | $I_2$ | 1.3 - 5.0 g/l | $kA[I_2]^{1/2}$ | 144 | 1.7 | -3 | 29 | 1.3 | 11 | * | (1) |
| .3 | *trans* - ICH:CHI (→ *cis*) | $C_{10}H_{18}$ | M/ml | 5 - 10 mole % | $I_2$ | 1.3 - 5.0 g/l | $kA[I_2]^{1/2}$ | 144 | 1.3 | -3 | 30 | 2.0 | 11 | * | (1) |

## COMMENTS

(.1) Dielectric constant measurements. Rate practically identical in the pure liquid and in the solvents listed. The photochemical reaction (2) in $C_{10}H_{18}$ (decalin) has an activation energy of $E$ = 13.4. (.2) (.3) Dielectric constant measurement. $A$ is assumed from the isotopic exchange reaction

$$cis\ (trans) - C_2H_2I_2 + \tfrac{1}{2}\ I_2^* \rightarrow cis\ (trans) - C_2H_2I^*I + \tfrac{1}{2}\ I_2;$$

$E$ is calculated from the assumed $A$ and the observed $k$. The rate of the photochemical reaction (1) in decalin solution is governed by the same law $k' A[I_2]^{1/2}$, with $k'$ proportional to the square root of the incident light intensity; $E$ = 11 kcal (77° - 114°C) for *cis* → *trans*, and = 13 kcal (77° - 114°C) for *trans* → *cis*.

## LITERATURE

(1) R.M.Noyes, R.G.Dickinson, Verner Schomaker *ACS* 1945, **67**, 1319. (2) R.E.Wood; see *ACS* 1945, **67**, 1327 footnote (15). (3) R.E.Wood, G.Dickinson *ACS* 1939, **61**, 3259.

# SYN-ANTI ISOMERIZATION

## C, H, O, N compounds, aromatic

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent (Medium) | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5C(=O)-C(=NOH)C_6H_5 \rightarrow C_6H_5C(=O)-C(=HON)C_6h_5$ <br> α-benzilmonoxime → β | pure liquid | HCl | 0.5 | *k* A | 55 | 6.98 | -5 |
| | | | | 1.0 | | 55 | 2.42 | -4 |
| | | | | 1.5 | | 55 | 4.87 | -4 |
| | | $H_2O + C_2H_5OH$ 96% | HCl | 0.5 | *k* A | 55 | 5.25 | -6 |
| | | | | 1.5 | | 55 | 3.54 | -5 |
| | | | | 2.0 | | 55 | 1.40 | -4 |
| | | | | 3.0 | | 55 | 7.52 | -4 |
| | | $H_2O + C_2H_5OH$ 96% | LiCl | 0.5 | *k* A | 55 | 2.79 | -5 |
| | | | | 1.5 | | 55 | 8.41 | -5 |
| | | | | 2.0 | | 55 | 2.46 | -4 |
| | | $H_2O + C_2H_5OH$ 96% | $N(CH_3)_4Cl$ | 0.5 | *k* A | 55 | 1.58 | -4 |
| | | $H_2O + C_2H_5OH$ 56% | HCl | 0.5 | *k* A | 55 | 5.38 | -7 |
| | | | | 1.5 | | 55 | 4.98 | -6 |
| | | $H_2O + C_2H_5OH$ 56% | KCl | 0.5 | *k* A | 55 | 3.19 | -5 |

## LITERATURE

T. W. J. Taylor, D. C. V. Roberts, *CSL* **1933**, 1439.

# BRANCHING ISOMERIZATION

*Liquid phase*

## Hydrocarbons

Rates and mass-action are in M/l per sec.

| No. | Reaction | Medium | Addend (Catalyst) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH_2CH_2CH_3 \rightarrow (CH_3)_2CHCH_3$ | pure liquid | (moles/mole A) | $kA[HAlBr_4]$ | | | | | | |
| | | | $Al_2Br_6$ 0.0118 + HBr 0.0077 | | 53.0 | 1.48 | -4 | | | |
| | | | 0.00418 0.0077 | | " | 1.70 | -4 | | | |
| | | | 0.0162 0.00096 | | 65.0 | 2.90 | -4 | | | |
| | | | 0.0077 0.0020 | | " | 2.80 | -4 | | | |
| | | | 0.0273 0.00543 | | " | 3.57 | -4 | | | |
| | | | 0.0056 0.0077 | | " | 2.73 | -4 | | | |
| | | | 0.0082 0.0077 | | " | 2.20 | -4 | | | |
| | | | 0.00666 0.0077 | | " | 2.88 | -4 | | | |
| | | | 0.00845 0.0077 | | 78.5 | 4.1 | -4 | 9.2 | 2.5 | 2 |
| .2 | $(CH_3)_2CHCH_3 \rightarrow CH_3CH_2CH_2CH_3$ | pure liquid | $Al_2Br_6$ 0.00968 + HBr 0.00204 | $kA[HAlBr_4]$ | 65.0 | 1.8 | -4 | | | |
| | | | 0.00965 0.00274 | | " | 1.9 | -4 | | | |
| | | | 0.0182 0.00644 | | " | 1.4 | -4 | | | |
| | | | 0.0214 0.0078 | | " | 1.5 | -4 | | | |
| | | | 0.00112 0.0078 | | " | 1.3 | -4 | | | |

## COMMENTS

(.1) (.2) Conversion in sealed tubes followed by vapor pressure and density determinations. Catalysts dissolved homogeneously except for slight solid residue on walls. Data of rates with varying amounts of $AlBr_3$ and HBr prove that the catalyst is $HAlBr_4$, and the rate proportional to its concentration. Consequently, $k$ was calculated on the basis of a rate law $kA[HAlBr_4]$, and shows sufficient constancy to bear out the conclusion. All data have been converted from M/ml to M/l.

## LITERATURE

P. A. Leighton, J. D. Heldman, *ACS* 1943, 65, 2276.

# ISOMERIZATION

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

## Hydrogen migration with Double bond shift

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_2{:}CHCH_2COO^- \rightarrow CH_3CH{:}CHCOO^-$ | $H_2O$ | 1.0 | NaOH | 1.05 | $k$A | 100 | 9.7 | -5 | * | (1) |
| .2 | $CH_3CH{:}CHCH_2COO^- \rightarrow CH_3CH_2CH{:}CHCOO^-$ | $H_2O$ | 1.0 | NaOH | 1.2 | $k$A | 100 | 1.9 | -6 | * | (2) |
| .3 | $CH_3CH_2CH{:}CHCOO^- \rightarrow CH_3CH{:}CHCH_2COO^-$ | $H_2O$ | 1.0 | NaOH | 1.2 | $k$A | 100 | 1.0 | -6 | * | (2) |

### COMMENTS

(.1) D exchange determined simultaneously. Proposed mechanism: $A + OH^- \rightarrow CH_2{:}CHCHCOO^- + H_2O \rightarrow L + OH^-$.

(.2) (.3) From the rate of establishment of the equilibrium

$$\begin{array}{ccc} CH_3CH_2CH{:}CHCOO^- & \rightleftharpoons & CH_3CH{:}CHCH_2COO^- \\ \rightleftharpoons & CH_3CH_2CHOHCH_2COO^- & \rightleftharpoons \end{array}$$

from $CH_3CH_2CH{:}CHCOO^-$.

### LITERATURE

(1) D.J.G.Ives, *CSL* **1938**, 91. (2) D.J.G.Ives, R.G.Kerlogue, *CSL* **1940**, 1362.

# ISOMERIZATION

*Liquid phase*

## Alkenyl group migration with Double bond shift on aliphatic C

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Medium | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH{:}CHC(CH_2{:}CHCH_2)(COOC_2H_5)_2 \rightarrow CH_3CH(CH_2{:}CHCH_2)CH{:}C(COOC_2H_5)_2$ | pure liquid | $kA$ | 193.1 | 1.43 | -4 | | | | (1) |
| .2 | $C_2H_5CH{:}CHC(CH_2{:}CHCH_2)(COOC_2H_5)_2 \rightarrow C_2H_5CH(CH_2{:}CHCH_2)CH{:}C(COOC_2H_5)_2$ | pure liquid | $kA$ | 193.1 | 1.84 | -4 | | | | (1) |
| .3 | $C_2H_5CH{:}C(CH_3)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow C_2H_5CH(CH_2{:}CHCH_2)C(CH_3){:}C(CN)(COOC_2H_5)$ | pure liquid | $kA$ | 176.5 | 1.35 | -3 | | | | (1) |
| .4 | $(CH_3)_2CHCH{:}C(CH_3)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow (CH_3)_2CHCH(CH_2{:}CHCH_2)C(CH_3){:}C(CN)(COOC_2H_5)$ | pure liquid | $kA$ | 180<br>200 | 3.54<br>1.40 | -4<br>-3 | 28.8<br>$\Delta S_a = -14.0$ | 2.3 | 10 | (2) |
| .5 | $C_4H_9CH{:}C(CH_3)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow C_4H_9CH(CH_2{:}CHCH_2)C(CH_3){:}C(CN)(COOC_2H_5)$ | pure liquid | $kA$ | 176.5 | 9.16 | -4 | | | | (1) |

| No. | Reaction | Medium | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $CH_3CH{:}C(C_2H_5)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow$ $CH_3CH(CH_2{:}CHCH_2)C(C_2H_5){:}C(CN)(COOC_2H_5)$ | pure liquid | $kA$ | 176.5 | 1.53 | -3 | | | | (1) |
| .7 | $CH_3CH{:}C(C_2H_5)C(CH_2{:}CHCH_2)(CN)_2 \rightarrow$ $CH_3CH(CH_2{:}CHCH_2)C(C_2H_5){:}C(CN)_2$ | pure liquid | $kA$ | 120 | 4.02 | -4 | | | | (2) |
| | | | | 130 | 9.12 | -4 | 25.8 | 8.7 | 10 | |
| | | | | 140 | 1.98 | -3 | | $\Delta S_a = -11.1$ | | |
| .8 | $CH_2{:}C(C_6H_5)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow$ $CH_2(CH_2{:}CHCH_2)C(C_6H_5){:}C(CN)(COOC_2H_5)$ | pure liquid | $kA$ | 176.5 | 1.60 | -3 | | | | (1) |

## COMMENTS

Refractive index measurements.

## LITERATURE

(1) A.C.Cope, R.E.Hoyle, D.Heyl, *ACS* 1941, **63**, 1843.

(2) E.Gordon Foster, A.C.Cope, Farrington Daniels, *ACS* 1947, **69**, 1893.

# ISOMERIZATION

*Liquid phase*

## Alkenyl group migration with Double bond shift on alicyclic ring

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Medium | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | |
| .1 | $C(CN)_2(CH_2{:}CHCH_2)$ - *cyclo* - $C_6H_9$ → | pure liquid | $kA$ | 120 | 1.81 | -4 | | | | (2) |
| | 1 - $(CH_2{:}CNCH_2)$ - 2 - $C(CN)_2$:*cyclo* - $C_6H_9$ | | | 130 | 4.09 | -4 | 26.2 | 6.3 | 10 | |
| | | | | 140 | 9.14 | -4 | | $\Delta S_a$ = -11.7 | | |
| .2 | $C(CN)(COOC_2H_5)(CH_2{:}CHCH_2)$ - *cyclo* - $C_6H_9$ → | pure liquid | $kA$ | 176.5 | 1.13 | -3 | | | | (1) |
| | 1 - $(CH_2{:}CHCH_2)$ - 2 - $C(CN)(COOC_2H_5)$:*cyclo* - $C_6H_9$ | | | | | | | | | |

## LITERATURE

(1) A.C.Cope, R.E.Hoyle, D.Heyl, *ACS* 1941, **63**, 1843.

(2) E.Gordon Foster, A.C.Cope, Farrington Daniels, *ACS* 1947, **69**, 1893.



942151 O—51——5

# ISOMERIZATION

*Liquid phase*

## OH group migration with Double bond shift

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH{:}CHCH(OH)C{:}CH \rightarrow CH_3CH(OH)CH{:}CHC{:}CH$ | $H_2O + C_2H_5OH$ 20 vol % | 0.0729 | HCl | 0.1 | $kA$ | 30 | 1.04 | -5 | |
| | | | | | 0.4 | | " | 5.46 | -5 | |
| | | | | | 1.0 | | " | 1.85 | -4 | |
| | | | | | 4.0 | | " | 6.18 | -3 | |
| | | | | | 0.1 | | 40 | 3.50 | -5 | |
| | | | | | 0.4 | | " | 2.03 | -4 | |
| | | | | | 1.0 | | " | 6.93 | -4 | |
| | | | | | 0.1 | | 50 | 1.07 | -4 | |
| | | | | | 0.4 | | " | 5.50 | -4 | 23.5 |
| | | | | | 1.0 | | " | 2.05 | -3 | 24.2 |
| | | | | | 0.1 | | 60 | 3.67 | -4 | 23.2 |
| | | | | $H_2SO_4$ | 0.2 | | 60 | 9.17 | -4 | 23.8 |
| | | | | $H_3PO_4$ | 1.0 | | " | 3.75 | -4 | 21.6 |
| | | | | $CH_3COOH$ | 1.0 | | " | 7.49 | -6 | 22.2 |
| | | 40 vol % | " | HCl | 0.1 | $kA$ | 30 | 3.49 | -6 | |
| | | | | | 0.4 | | " | 1.75 | -5 | |
| | | | | | 1.0 | | " | 7.19 | -5 | |
| | | | | | 4.0 | | " | 2.40 | -3 | |

| No. | Reaction | Solvent | AAmount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperarure | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH{:}CHCH(OH)C{:}CH \rightarrow CH_3CH(OH)CH{:}CHC{:}CH$ *(continued)* | $H_2O + C_2H_5OH$ 40 vol % | | | 0.1 | | 40 | 1.28 | -5 | |
| | | | | | 0.4 | | " | 5.64 | -5 | |
| | | | | | 1.0 | | " | 2.73 | -4 | |
| | | | | | 0.1 | | 50 | 3.67 | -5 | |
| | | | | | 0.4 | | " | 2.49 | -4 | 25.1 |
| | | | | | 1.0 | | " | 8.63 | -4 | 24.7 |
| | | | | | 0.1 | | 60 | 9.48 | -5 | 22.7 |
| | | | | $H_2SO_4$ | 0.2 | | 60 | 3.35 | -4 | |
| | | | | $H_3PO_4$ | 1.0 | | " | 1.11 | -4 | |
| | | | | $CH_3COOH$ | 1.0 | | " | 1.65 | -6 | |
| | | 60 vol % | | HCl | 0.1 | $k$ A | 30 | 9.71 | -7 | |
| | | | | | 0.4 | | " | 5.43 | -6 | |
| | | | | | 1.0 | | " | 2.55 | -5 | |
| | | | | | 4.0 | | " | 1.77 | -3 | |
| | | | | | 0.1 | | 40 | 3.71 | -6 | |
| | | | | | 0.4 | | " | 2.27 | -5 | |
| | | | | | 1.0 | | " | 8.30 | -5 | |
| | | | | | 0.1 | | 50 | 1.35 | -5 | |
| | | | | | 0.4 | | " | 7.16 | -5 | 24.7 |
| | | | | | 1.0 | | " | 2.87 | -4 | 25.8 |
| | | | | | 0.1 | | 60 | 4.68 | -5 | 25.7 |
| | | | | $H_2SO_4$ | 0.2 | | 60 | 1.24 | -4 | |
| | | | | $H_3PO_4$ | 1.0 | | " | 2.63 | -5 | |
| | | | | $CH_3COOH$ | 1.0 | | " | 4.17 | -7 | |

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH{:}CHCH(OH)C{:}CH \rightarrow CH_3CH(OH)CH{:}CHC{:}CH$ *(continued)* | $H_2O + C_2H_5OH$ 80 vol % | | HCl | 0.1 | $k$ A | 30 | 3.50 | −7 | |
| | | | | | 0.4 | | " | 1.87 | −6 | |
| | | | | | 1.0 | | " | 8.46 | −6 | |
| | | | | | 0.1 | | 40 | 1.42 | −6 | |
| | | | | | 0.4 | | " | 7.62 | −6 | |
| | | | | | 1.0 | | " | 3.64 | −5 | |
| | | | | | 0.1 | | 50 | 5.33 | −6 | |
| | | | | | 0.4 | | " | 3.33 | −5 | 27.2 |
| | | | | | 1.0 | | " | 1.21 | −4 | 26.5 |
| | | | | | 0.1 | | 60 | 1.67 | −5 | 25.7 |
| | | | | $H_2SO_4$ | 0.2 | | 60 | 5.38 | −5 | |
| | | | | $H_3PO_4$ | 1.0 | | " | 4.53 | −6 | |
| | | | | $CH_3COOH$ | 1.0 | | " | 3.33 | −8 | |
| | | $C_2H_5OH$ | | HCl | 1.0 | $k$ A | 30 | 7.84 | −5 | |
| | | | | | | | 40 | 2.60 | −4 | |
| | | | | | | | 50 | 7.84 | −4 | 22.5 |
| | | | | $CH_3COOH$ | 1.0 | | 60 | 2.33 | −8 | |
| | | $H_2O$ | | $CH_3COOH$ | 1.0 | | 60 | 2.38 | −5 | |

## COMMENTS

Spectrophotometric determinations. Up to 80 vol % $C_2H_5OH$, and except with high HCl ( = 4 M/l), the rate constant is related to dielectric constant $\epsilon$ by $\log k = m\epsilon + n$, with the following values of $m$ and $n$ ($k$ in $sec^{-1}$):

| *Catalyst* | | *Temperature* | $10^2 m$ | $n$ |
|---|---|---|---|---|
| HCl | 0.1 | 30 | 4.69 | -4.17 |
| | 0.4 | " | 4.39 | -3.27 |
| | 1.0 | " | 3.85 | -1.197 |
| | 0.1 | 40 | 4.68 | -3.347 |
| | 0.4 | " | 4.44 | -2.573 |
| | 1.0 | " | 4.19 | -1.873 |
| | 0.1 | 50 | 4.20 | -2.601 |
| | 0.4 | " | 3.93 | -1.853 |
| | 1.0 | " | 4.00 | -1.166 |
| | 0.1 | 60 | 3.93 | -1.897 |
| $H_2SO_4$ | 0.2 | 60 | 3.74 | -1.346 |
| $H_3PO_4$ | 1.0 | 60 | 5.28 | -2.580 |
| $CH_3COOH$ | 1.0 | 60 | 6.21 | -4.76 |

The rearrangement of the oxonium ion $AH^+$ is considered to be rate determining.

Previous data of E. R. H. Jones, J., T. McCombie, *CSL* **1943**, 261, vitiated by heterogeneity, are not included.

## LITERATURE

E. A. Braude, E. R. H. Jones, *CSL* **1944**, 436; E. A. Braude, *CSL* **1944**, 443.

# ISOMERIZATION

## H Substitution by $NH_2$ from side chain in aromatic ring

*Liquid phase*

Amounts are in M/1000 g

Rates are in M/1000 g per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5NH{\cdot}N_2{\cdot}C_6H_5 \rightarrow p\text{-}NH_2C_6H_4{\cdot}N_2{\cdot}C_6H_5$ | $C_6H_5NH_2$ | 0.25 | HCl | 0.025 | $k$ A | 25 | 1.08 | -6 |
| | | | | | 0.05 | | " | 2.05 | -6 |
| | | | | | 0.1 | | " | 4.39 | -6 |
| | | | | | 0.025 | " | 45 | 1.51 | -5 |
| | | | | | 0.05 | | " | 2.93 | -5 |
| | | | | | 0.1 | | " | 5.72 | -5 |
| | | | | | 0.2 | | " | 1.15 | -4 |
| | | | " | HBr | 0.025 | " | 25 | 1.72 | -6 |
| | | | | | 0.05 | | " | 3.67 | -6 |
| | | | | | 0.1 | | " | 7.86 | -6 |
| | | | | | 0.025 | " | 45 | 2.33 | -5 |
| | | | | | 0.05 | | " | 4.83 | -5 |
| | | | | | 0.1 | | " | 1.05 | -4 |
| | | | | | 0.2 | | " | 2.32 | -4 |
| | | " | " | $HNO_3$ | 0.025 | " | 25 | 1.41 | -6 |
| | | | | | 0.05 | | " | 2.87 | -6 |
| | | | | | 0.1 | | " | 6.06 | -6 |
| | | | | | 0.025 | " | 45 | 1.98 | -5 |
| | | | | | 0.05 | | " | 4.18 | -5 |
| | | | | | 0.1 | | " | 8.39 | -5 |

2

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5NH{\cdot}N_2{\cdot}C_6H_5 \rightarrow p\text{-}NH_2C_6H_4{\cdot}N_2{\cdot}C_6H_5$ *(continued)* | $C_6H_5NH_2$ | 0.25 | $o\text{-}OHC_6HCOOH$ | 0.025 | $k$ A | 25 | 1.85 | -7 |
| | | | | | 0.05 | | " | 4.21 | -7 |
| | | | | | 0.1 | | " | 1.00 | -6 |
| | | | | | 0.2 | | " | 2.41 | -6 |
| | | | " | | 0.025 | " | 45 | 2.05 | -6 |
| | | | | | 0.05 | | " | 4.46 | -6 |
| | | | | | 0.1 | | " | 1.02 | -5 |
| | | | | | 0.2 | | " | 2.62 | -5 |
| | | " | " | $o\text{-}NO_2C_6H_4COOH$ | 0.025 | " | 45 | 1.17 | -6 |
| | | | | | 0.05 | | " | 2.60 | -6 |
| | | | | | 0.1 | | " | 6.22 | -6 |
| | | " | " | $m\text{-}NO_2C_6H_4COOH$ | 0.025 | " | 45 | 2.46 | -7 |
| | | | | | 0.05 | | " | 6.33 | -7 |
| | | | | | 0.1 | | " | 1.55 | -6 |
| | | | " | $o\text{-}BrC_6H_4COOH$ | 0.025 | " | 45 | 2.90 | -7 |
| | | | | | 0.05 | | " | 5.53 | -7 |
| | | | | | 0.1 | | " | 1.42 | -6 |
| | | | | | 0.2 | | " | 4.16 | -6 |
| | | $p\text{-}CH_3C_6H_4NH_2$ | 0.25 | HBr | 0.1 | " | 45 | 1.08 | -5 |
| | | | | HCl | " | | " | 6.78 | -6 |
| | | | | $(NO_3)_3C_6H_2OH$ | " | | " | 1.41 | -5 |
| | | | | $o\text{-}NO_2C_6H_4COOH$ | " | | " | 1.11 | -6 |
| | | | | $m\text{-}NO_2C_6H_4COOH$ | " | | " | 3.96 | -7 |
| | | | | $o\text{-}BrC_6H_4COOH$ | " | | " | 3.88 | -7 |

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5NH \cdot N_2 \cdot C_6H_5 \rightarrow p\text{-}NH_2C_6H_4 \cdot N_2 \cdot C_6H_5$ *(continued)* | $m\text{-}ClC_6H_4NH_2$ | 0.25 | HBr | 0.1 | $kA$ | 25 | 4.74 | −5 |
| | | | | $o\text{-}NO_2C_6H_4COOH$ | " | | " | 9.64 | −7 |
| | | | | $m\text{-}NO_2C_6H_4COOH$ | " | | " | 1.85 | −7 |
| | | | | $o\text{-}BrC_6H_4COOH$ | " | | " | 1.66 | −7 |

## COMMENTS

In $C_6H_5NH_2$, at 45° C, $k$ can be represented as a function of the concentration $c$ of the catalyst, by $k = ac + bc^2$, with the following empirical values of $a$ and $b$:

| *Catalyst* | $a$ | $b$ |
|---|---|---|
| HCl, HBr | $9.11 \times 10^{-4}$ | $1.27 \times 10^{-3}$ |
| $o\text{-}OHC_6H_4COOH$ | $7.60 \times 10^{-5}$ | $2.63 \times 10^{-4}$ |
| $o\text{-}NO_2C_6H_4COOH$ | $4.15 \times 10^{-5}$ | $2.07 \times 10^{-4}$ |
| $m\text{-}NO_2C_6H_4COOH$ | $9.52 \times 10^{-6}$ | $6.20 \times 10^{-5}$ |
| $o\text{-}BrC_6H_4COOH$ | $7.79 \times 10^{-6}$ | $6.39 \times 10^{-5}$ |

Other acids in original.

## LITERATURE

H. Goldschmidt, R. W. Reinders, *BDC* 1896, **29**, 1369, 1899; H. Goldschmidt, S. Johnsen, E. Overwein, *ZPC* 1924, **110**, 251; H. Goldschmidt, *ZEC* 1930, **36**, 662.

# ISOMERIZATION

*Liquid phase*

## H substitution by halogen (X) from NX group in aromatic ring

Amounts are in M/1000 g.

Rates are per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5NICHO \rightarrow p\text{-}IC_6H_4NH$ | $C_6H_5OCH_3$ | 0.010 | $CH_2ClCOOH$ | 0.297 | $kA$ | 25 | 1.32 | -4 |
| | | | | | 1.26 | | " | 6.15 | -4 |
| | | " | " | $CHCl_2COOH$ | 0.381 | " | 25 | 2.34 | -4 |
| | | | | | 0.926 | | " | 6.41 | -4 |
| | | " | " | $(CH_3)_3CCOOH$ | 2.46 | " | 25 | 4.02 | -4 |
| | | | | | 5.84 | | " | 9.38 | -4 |
| | | " | " | $C_6H_5COOH$ | 1.85 | " | 25 | 2.38 | -4 |
| | | | | | 7.98 | | " | 1.15 | -3 |
| | | | | $o\text{-}NO_2C_6H_4COOH$ | 0.523 | " | 25 | 2.34 | -4 |
| | | | | | 1.13 | | " | 5.94 | -4 |
| | | | | $m\text{-}NO_2C_6H_4COOH$ | 0.704 | " | 25 | 1.11 | -4 |
| | | | | | 3.16 | | " | 1.17 | -3 |
| | | | | $C_6H_5CH{:}CHCOOH$ | 1.49 | " | 25 | 1.53 | -4 |
| | | | | | 6.94 | | " | 6.98 | -4 |
| | | | | $2,4,6\text{-}Cl_3C_6H_4COOH$ | 4.06 | " | 25 | 4.60 | -4 |
| | | | | | 8.12 | | " | 6.13 | -4 |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .2 | $C_6H_5NClCOCH_3 \rightarrow o,p\text{-}ClC_6H_4NHCOCH_3$ | $C_6H_5Cl$ | 0.005 | $CH_2ClCOOH$ | 0.116 | $kA$ | 100 | 5.76 | -6 |
| | | | | | 0.466 | | " | 2.53 | -5 |
| | | | " | $CHCl_2COOH$ | 0.097 | " | 100 | 2.18 | -5 |
| | | | | | 0.499 | | " | 1.64 | -4 |
| | | | | $o\text{-}NO_2C_6H_4COOH$ | 0.047 | " | 100 | 8.41 | -6 |
| | | | | | 0.156 | | " | 2.80 | -5 |
| | | | | $p\text{-}NO_2C_6H_4COOH$ | 0.112 | " | 100 | 1.53 | -6 |
| | | | | | 0.430 | | " | 1.11 | -5 |
| | | | | $C_6H_5CH_2COOH$ | 0.456 | " | 100 | 6.13 | -6 |
| | | | | | 1.043 | | " | 1.80 | -5 |

## COMMENTS

Initially first order; (.1) self-accelerating or self-inhibiting, (.2) self-accelerating owing to formation of traces of · HCl.

## LITERATURE

R. P. Bell, P. V. Danckwerts, *CSL* **1939**, 1774.

# ISOMERIZATION

## Beckmann rearrangement



Reaction type

$$\underset{\underset{NOX}{\|}}{ArCR} \xrightarrow{(slow)} \underset{\underset{RN}{\|}}{ArCOX} \xrightarrow{(fast)} \underset{\underset{RNX}{|}}{ArCO} \quad \text{(end product)}$$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5\underset{\underset{NOC_6H_2(NO_2)_3}{\|}}{C}CH_3 \rightarrow C_6H_5\underset{\underset{CH_3NC_6H_2(NO_2)_3}{\|}}{C}O$ | $CCl_4$ | 0.043 | | | $kA$ | 99.3 | 1.30 | -5 | | ([1]) |
| | | | | | | | 116 | 6.5 | -5 | ~ 27 | |
| | | $C_6H_6$ | " | | | " | 85 | 2.88 | -5 | | " |
| | | | | | | | 99.1 | 1.26 | -4 | ~ 27 | |
| | | $CH_3Cl$ | " | | | " | 75 | 6.5 | -5 | | " |
| | | | | | | | 85 | 1.92 | -4 | ~ 27 | |
| | | $C_2H_4Cl_2$ | | | | " | 65 | 6.8 | -5 | | " |
| | | | | | | | 75 | 2.04 | -4 | | |
| | | | | | | | 85 | 5.8 | -4 | ~ 27 | |
| | | $CH_3CN$ | | | | " | 60 | 1.03 | -4 | | " |
| .2 | $C_6H_5\underset{\underset{NOC_6H_2(NO_2)_3}{\|}}{C}C_6H_5 \rightarrow C_6H_5\underset{\underset{C_6H_5NC_6H_2(NO_2)_3}{\|}}{C}O$ | $CCl_4$ | 0.078 | | | $kA$ | 75 | 3.18 | -5 | | ([1]) |
| | | | | | | | 85 | 9.6 | -5 | | |
| | | | | | | | 99.7 | 4.8 | -4 | ~ 27 | |
| | | $C_6H_6$ | | | | " | 50 | 9.2 | -6 | | " |
| | | | | | | | 70 | 1.19 | -4 | | |
| | | | | | | | 75 | 2.18 | -4 | | |
| | | | | | | | 79 | 3.37 | -4 | ~ 27 | |

162.455

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $C_6H_5CC_6H_5$ (‖ $NOC_6H_2(NO_2)_3$) → $C_6H_5CO$ (| $C_6H_5NC_6H_2(NO_2)_3$) | $CHCl_3$ | | | | $kA$ | 40 | 4.5 | -5 | | (1) |
| | | | | | | | 45 | 8.8 | -5 | | |
| | | | | | | | 50 | 1.5 | -4 | | |
| | | | | | | | 55 | 2.4 | -4 | | |
| | | | | | | | 60 | 4.0 | -4 | | |
| | *(continued)* | $C_2H_4Cl_2$ | | | | | 50 | 3.2 | -4 | | " |
| | | $CCl_4$ | 0.0225 | | | $kA$ | 70.5 | 1.84 | -5 | | (2) |
| | | | | | | | 80.5 | 5.87 | -5 | | |
| | | | | | | | 81.0 | 6.30 | -5 | | |
| | | | | | | | 92.8 | 2.10 | -4 | | |
| | | | | | | | 100.0 | 4.30 | -4 | | |
| | | $CCl_4$ | | | $kA$; $k = k_o + aA$ | | | $k_o$ | | $10^5a$ | (2) |
| | | | 0.0225 | | | | 70.5 | (1.17) | -5 | | |
| | | | ~ 0.01 - 0.03 | | | | 80.5 | 4.40 | -5 | 67 | |
| | | | " | | | | 81.0 | 4.73 | -5 | 67 | |
| | | | " | | | | 85.9 | 7.9 | -5 | | |
| | | | " | | | | 92.8 | 1.68 | -4 | 190 | |
| | | | " | | | | 100.0 | 3.41 | -4 | 392 | |
| | | " | 0.0225 | $c$ = | $kA$; $k=k_o + ac + bc^2$ | | | $k_o$ | | $10^5a$ | $10^5b$ |
| | | | | $CH_3CN$ | 0.3 - 0.6 | | 81.0 | 4.73 | -5 | 52 | 24 |
| | | | | $(CH_3)_2CO$ | 0.25 - 0.5 | | " | " | | 25 | 9.5 |
| | | | | $C_4H_9Cl$ | 0.38 - 0.73 | | " | " | | 5.3 | |
| | | " | 0.0225 | $CH_3NO_2$ | 0.0 - 1.0 | | 70.5 | 1.17 | -5 | 13.3 | 13 |
| | | | | | | | 81.0 | 4.73 | -5 | 36.5 | 39 |
| | | | | | | | 92.8 | 1.68 | -4 | 118 | 80 |
| | | " | 0.0225 | $C_2H_4Cl$ | 0.0 - 0.96 | | 81.0 | 4.73 | -5 | 6.8 | 2.4 |
| | | | | | 0.0 - 0.8 | | 91.0 | | | 17.8 | 6.1 |
| | | | | | 0.0 - 0.38 | | 100.1 | | | 40.5 | 9.3 |

## COMMENTS

The increase of the first-order $k$ with the concentration of A indicates self-catalysis by A itself, representable by $k = k_o + a\,A$ ([2]). In the presence of extraneous catalysts (concentration $c$), $k = k_o + ac + bc^2$, where $k_o$ = rate constant of the uncatalyzed reaction. Data for further catalysts in original ([2]).

## LITERATURE

([1]) A. W. Chapman, C. C. Howis, *CSL* **1933**, 806.

([2]) A. W. Chapman, *CSL* **1934**, 1550.

# ISOMERIZATION

## Double bond to Closed ring

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3)_2C{:}CHCOCH{:}C(OH)COOCH_3 \rightarrow (CH_3)_2\underbrace{CCH_2COCH{:}CCOOCH_3}_{O}$ | $C_6H_5Cl$ | 0.01 | X = | $k\,A;\ k = k_c k'X/(k' + k_cX) + aX$ | | 99.0 | | |
| | | | | $(C_2H_5)_3N$ | 0.003 - 0.1 | | $k_c$ | 2.37 | -3 |
| | | | | | | | $k'$ | 1.67 | -4 |
| | | | | | | | $a$ | 0 | |
| | | | | $(CH_3)_3N$ | 0.01 - 0.2 | | $k_c$ | 3.43 | -3 |
| | | | | | | | $k'$ | 3.00 | -4 |
| | | | | | | | $a$ | 0 | |
| | | | | $C_6H_5CON(C_2H_5)_2$ | 0.05 - 0.35 | | $k_c$ | 1.97 | -4 |
| | | | | | | | $k'$ | 1.12 | -4 |
| | | | | | | | $a$ | 0 | |
| | | | | $CHCl_2COOH$ | 0.001 - 0.2 | | $k_c$ | 4.18 | -1 |
| | | | | | | | $k'$ | 2.42 | -3 |
| | | | | | | | $a$ | 1.17 | -3 |
| | | | | $o\text{-}NO_2C_6H_4COOH$ | 0.001 - 0.008 | | $k_c$ | 1.92 | -1 |
| | | | | | | | $k'$ | 2.39 | -4 |
| | | | | | | | $a$ | 0 | |
| | | | | $C_6H_5COOH$ | 0.003 - 0.2 | | $k_c$ | 4.18 | -2 |
| | | | | | | | $k'$ | 2.29 | -4 |
| | | | | | | | $a$ | 0 | |



942151 O—51——6

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3)_2C{:}CHCOCH{:}C(OH)COOCH_3 \rightarrow (CH_3)_2CCH_2COCH{:}CCOOCH_3$ (O) *(continued)* | $C_6H_5Cl$ | 0.01 | X = $CH_3COOH$ | $kA$; $k = k_c k'X/(k' + k_cX) + aX$ 0.003 - 0.2 | | $k_c$ 1.78<br>$k'$ 2.22<br>$a$ 0 | | -2<br>-4 |

## COMMENTS

Selected bases and acids For basic catalysts and weak acids, $a = 0$. For basic catalysts, $k$ are corrected for heterogeneous catalysis by glass; for acid catalysts, $k$ are corrected for the heterogeneous inhibition by glass.

## LITERATURE

R. P. Bell, S. M. Rybicka, *CSL* 1947, 24.

# ISOMERIZATION

## Ring closing - Ionization

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

Reaction type $ClCH_2(CH_2)_nSC_2H_5 \rightarrow [\underbrace{CH_2(CH_2)_n}\overset{+}{S}C_2H_5]Cl^-$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $ClCH_2CH_2CH_2CH_2CH_2SC_2H_5$ | $H_2O + (CH_3)_2CO$ 50 % | 0.024 | *k* A | 68.6 | 7.5 | -5 |
| | | | | | 80.4 | 1.8 | -4 |
| | | | | | 88.6 | 3.8 | -4 |
| | | | | | (100) | (8.8) | -4 |
| .2 | $ClCH_2CH_2CH_2CH_2CH_2CH_2SC_2H_5$ | $H_2O + (CH_3)_2CO$ 50 % | 0.0014 - 0.025 | *k* A | 100 | 1.17 | -4 |
| | | | | | 116 | 4.54 | -4 |

### COMMENTS

Analysis for $Cl^-$. (.1) *k* at 100°C extrapolated.

### LITERATURE

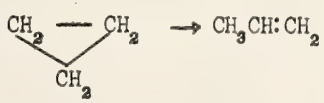
G. M. Bennett, E. G. Turner, *CSL* **1938**, 813.

# ISOMERIZATION

*Gas phase*

## Ring opening to Double bond

Amounts are in mm Hg. Rates and rate constants are per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 |  | 600 | $kA$ | 440 | 1.5 | -4 | | | | * | (1)(2) |
| | | " | | 480 | 1.9 | -4 | | | | | |
| | | " | | 500 | 5.6 | -4 | | | | | |
| | | " | | 520 | 1.7 | -3 | 65.0 | 2 | 15 | | (1) |
| | | 910 | $kA$ | 500 | 5.7 | -4 | | | | * | (2) |
| | | 703 | | " | 5.9 | -4 | | | | | (1) |
| | | 600 | | " | 5.6 | -4 | | | | | (2) |
| | | 383 | | " | 6.3 | -4 | | | | | (1) |
| | | 251 | | " | 5.2 | -4 | | | | | (2) |
| | | 109 | | " | 5.1 | -4 | | | | | (2) |
| | | 10 | | " | 3.4 | -4 | | | | | (2) |

## COMMENTS

Selected values. Proof of homogeneity given. $H_2$, $C_2H_4$, $C_3H_8$, have little effect on the rate. Decomposing $C_4H_{10}$ accelerates the reaction. Data of (1) in essential agreement with (2). Rate-determining step assumed to be (1) $A \rightarrow -CH_2CH_2CH_2-$, followed by (2) $-CH_2CH_2CH_2- \rightarrow A$, (3) $-CH_2CH_2CH_2- \rightarrow L$, (4) $-CH_2CH_2CH_2 + A \rightarrow 2L$; $-dA/dt = k_1A\,(k_3 + 2k_4A)/(k_2 + k_3 + k_4A)$.

## LITERATURE

(1) Chambers, G.B.Kistiakowsky, *ACS* 1934, 56, 399.

(2) E.S.Corner, R.N.Pease, *ACS* 1945, **67**, 2067.

# ESTERIFICATION

*Gas phase*

## Aliphatic acid anhydride + Alcohol

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH$ | $10^3A$ = 2.32 ; | $10^3B$ = 2.68 | $k$AB | 79.2 | 2.1 | -3 |
| | | 5.64 | 5.13 | | " | 8.5 | -3 |
| | | 4.42 | 11.61 | | " | 1.79 | -2 |
| | | 27.19 | 30.18 | | " | 1.56 | -2 |
| | | 39.08 | 24.77 | | " | 1.18 | -2 |
| | | 43.43 | 43.60 | | " | 2.52 | -2 |

### COMMENTS

No marked change of $k$ by change of the surface/volume ratio.

### LITERATURE

E. A. Moelwyn-Hughes, C. N. Hinshelwood, *CSL* **1932**, 230.

# ESTERIFICATION

## Aliphatic carboxylic acid + Alcohol

*Liquid phase*

Reaction type $RCOOH + R'OH \rightarrow RCOOR' + H_2O$
(A) (B) (L) (M)

Rate measured $-dA/dt = +dL/dt$

G* = Goldschmidt equation, $kA[H^+]r/(M + r)$; $r = [BH^+][M]/[MH^+]$

All rates are in M/l per sec.
All amounts in M/l.

Comments, Literature, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 0 | 1.84 | -1 | 0.11 | | | | * | (14) |
| | | | | | | | 20 | 6.32 | -1 | 0.20 | | | | | " |
| | | | | | | | 30 | 1.10 | 0 | 0.25 | | | | | " |
| | | | | | | | 40 | 1.73 | 0 | 0.32 | 10.0 | 1.7 | 7 | | " |
| .2 | $CH_3COOH + CH_3OH$ | B | 0.1 | HCl | 0.005 | G* | 20 | 4.93 | -2 | 0.20 | | | | * | (19) |
| | | | | | | | 30 | 9.02 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 1.53 | -1 | 0.32 | | | | | " |
| | | | | | | | 50 | 2.48 | -1 | 0.42 | 10.2 | | | | " |
| | | B | 0.5 | HCl | 0.001 - 0.005 | | 0 | 1.18 | -2 | 0.15 | | | | | (19) |
| | | | | | | G* | 14 | 3.25 | -2 | 0.18 | | | | | " |
| | | | | | | | 20 | 4.41 | -2 | 0.20 | | | | (14) | " |
| | | | | | | | 25 | 6.01 | -2 | 0.22 | | | | | " |
| | | | | | | | 30 | 7.99 | -2 | 0.25 | | | | (14) | " |
| | | | | | | | 35 | 1.04 | -1 | 0.31 | | | | | " |
| | | | | | | | 40 | 1.32 | -1 | 0.32 | | | | (14) | " |
| | | | | | | | 45 | 1.68 | -1 | 0.49 | | | | | " |
| | | | | | | | 50 | 2.14 | -1 | 0.42 | 10.2 | 1.2 | 6 | (14) | " |
| | | | | | | | 100 | 1.89 | 0 | | 10.2 | 1.8 | 6 | | (9) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3COOH + CH_3OH$ *(continued)* | B | 1.0 | HCl | 0.001 - 0.005 | G* | 0 | 1.06 | -2 | 0.15 | | | | * | (19) |
| | | | | | | | 14 | 2.89 | -2 | 0.18 | | | | | " |
| | | | | | | | 25 | 5.52 | -2 | 0.22 | | | | | " |
| | | | | | | | 45 | 1.47 | -1 | 0.49 | | | | | " |
| | | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | * | (2) |
| | | 0 | | HCl | 0.05 | | 25 | 6.20 | -2 | 0.21 | | | | * | (2) |
| | | 1 | | | | | 25 | 9.75 | -3 | 0.21 | | | | | " |
| | | 2 | | | | | 25 | 4.85 | -3 | 0.21 | | | | | " |
| .3 | $CH_3COOH + CH_3OH$ | B | 0.1 - 1.0 | | - | $kA^2$ | 25 | 2.13 | -7 | - | | | | | (13) |
| | | | | | | | 70 | 4.13 | -6 | | | | | | " |
| | | | | | | | 100 | (7.6) | -6 | | (13.0) | (3.4) | | | (9) |
| | | | | | | | 109 | 1.47 | -5 | | | | | | (13) |
| | | | | | | | 151 | 6.06 | -5 | | | | | | " |
| | | B | 0.1 - 1.0 | Buffer | | $kA^2 + 0.032k$ | | | | | | | | | (13) |
| | | | | | | | 70 | 1.38 | -6 | - | | | | | " |
| | | | | | | | 100 | 9.46 | -6 | | | | | | " |
| | | | | | | | 109 | 1.83 | -5 | | | | | | " |
| | | | | | | | 151 | 1.53 | -4 | | 13.0 | | | | " |
| | | PhOMe | " | - | - | $kA^{1.5}B$ | | | | | 11.0 | | | | (13) |
| .4 | $CH_3COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 1.56 | -2 | | | | | * | (3) |
| .5 | $CH_3COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 5.7 | -6 | - | 15.2 | 4.9 | 3 | * | (1) |
| | | $H_2O$ | 1.0 | - | - | $kAB$ | 50 | 2.34 | -7 | - | | | | | (12) |
| | | | | | | | 60 | 4.20 | -7 | | | | | | " |
| | (see Supplementary Table) | | | | | | 70 | 7.98 | -7 | | | | | | " |
| | | | | | | | 75 | 1.27 | -6 | | 13.8 | 4.6 | 2 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $\tau$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $CH_3COOH + C_3H_7OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 2.74 | -3 | 0.11 | | | | * | (6) |
| | | 0.1 | | | " | | " | 2.63 | -3 | " | | | | | " |
| | | 0.5 | | | " | | " | 2.30 | -3 | " | | | | | " |
| | | 1.0 | | | " | | " | 2.23 | -3 | " | | | | | " |
| .7 | $CH_3COOH + (CH_3)_2CHOH$ | B | 1.0 | - | - | $kA^2$ | 100 | 1.65 | -6 | - | | | | | (9) |
| | | | | | | | 119 | 4.49 | -6 | | | | | | " |
| | | | | | | | 139 | 1.19 | -5 | | | | | | " |
| | | | | | | | 154 | 2.32 | -5 | | | | | | " |
| | | | | | | | 184 | 7.29 | -5 | | 15.3 | 1.6 | 3 | | " |
| .8 | $CH_3COOH + C_4H_9OH$ | $H_2O$ | | - | - | $kAB$ | 70 | 1.04 | -6 | - | | | | | (12) |
| | | | | | | | 75 | 1.31 | -6 | | | | | | " |
| | (see Supplementary Table) | | | | | | 80 | 1.73 | -6 | | 13.7 | 5.7 | 2 | | " |
| .9 | $CH_3COOH + (CH_3)_2CHCH_2OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 1.31 | -3 | 0.089 | | | | * | (5) |
| | | 0.4 | | | " | | " | 1.25 | -3 | " | | | | | . |
| | | 2.0 | | | " | | " | 1.46 | -3 | " | | | | | |
| .10 | $CH_3COOH + (C_2H_5)(CH_3)CHOH$ | $H_2O$ | | - | - | $kAB$ | 70 | 1.77 | -7 | - | | | | | (12) |
| | | | | | | | 75 | 2.68 | -7 | | | | | | " |
| | | | | | | | 80 | 3.89 | -7 | | 17.5 | 2.5 | 4 | | " |
| .11 | $CH_3COOH + (CH_3)_3COH$ | B | 1.0 | - | - | $kA^2$ | 100 | 2.50 | -8 | - | | | | * | (9) |
| | | | | | | | 140 | 2.86 | -7 | | | | | | " |
| | | | | | | | 154 | 5.95 | -7 | | | | | | " |
| | | | | | | | 183 | 1.81 | -6 | | | | | | " |
| | | | | | | | 211 | 8.35 | -6 | | 18.8 | 2.7 | 3 | | " |

202.441.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .12 | $CH_3COOH$ + *cyclo*-$C_6H_{11}OH$ | B | 1.0 | – | – | $kA^2$ | 100 | 3.18 | -6 | – | 16.6 | 1.8 | 4 | | (1) |
| .13 | $CH_3COOH + C_6H_5CH_2OH$ | B | 1.0 | – | – | $kA^2$ | 100 | 7.1 | -6 | – | | | | | (9) |
| | | | | | | | 119 | 2.08 | -5 | | | | | | " |
| | | | | | | | 140 | 5.82 | -5 | | | | | | " |
| | | | | | | | 154 | 9.49 | -5 | | 15.3 | 7.3 | 3 | | " |
| .14 | $(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH$ | B | 0.1 - 0.2 | – | – | $kA$ | 50 | 8.0 | -5 | – | 18.8 | | | | (11) |
| | | | | | | | 75 | 6.6 | -4 | | | | | | |
| | | $C_6H_{14}$ | 0.158 | – | – | $kAB$ | 50 | 1.62 | -4 | – | | | | * | (10) |
| | | | | | | | 60 | 3.84 | -4 | | | | | | " |
| | | | | | | | 70 | 1.02 | -3 | | | | | | " |
| | | | | | | | 100 | 2.66 | -3 | | 12.4 | | | | " |
| | | $CCl_4$ | 0.1 | – | – | $kAB$ | 50 | 2.6 | -4 | – | | | | * | (10) |
| | | | | | | | 60 | 6.28 | -4 | | | | | | " |
| | | | | | | | 70 | 1.14 | -3 | | | | | | " |
| | | | | | | | 100 | 4.50 | -3 | | 13.2 | | | | " |
| .15 | $CH_2OHCOOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 2.16 | -2 | | | | | | (3) |
| .16 | $CCl_3COOH + C_6H_5CH_2OH$ | B | 1.0 | – | – | $kA^2$ | 24 | 2.94 | -6 | – | | | | * | (9) |
| | | | | | | | 35 | 6.42 | -6 | | | | | | " |
| | | | | | | | 53 | 2.11 | -5 | | | | | | " |
| | | | | | | | 65 | 4.73 | -5 | | | | | | " |
| | | | | | | | 78 | 9.15 | -5 | | | | | | " |
| | | | | | | | 100 | 2.76 | -4 | | 13.1 | 1.5 | 4 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .17 | $C_2H_5COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | $G^*$ | 20 | 4.00 | -2 | 0.20 | | | | * | (14) |
| | | | | | | | 25 | 5.73 | -2 | 0.22 | | | | | " |
| | | | | | | | 30 | 6.70 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 1.11 | -1 | 0.32 | | | | | " |
| | | | | | | | 50 | 1.93 | -1 | 0.42 | 10.0 | 1.0 | 6 | | " |
| | | B | 0.1 | HCl | 0.002 - 0.006 | | 20 | (3.8) | -2 | 0.18 | (11.6) | (9.1) | 5 | * | (1) |
| | | | | | | $G^*$ | 20 | 4.23 | -2 | 0.20 | | | | | (17) |
| | | | | | | | 30 | 7.58 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 1.31 | -1 | 0.34 | | | | | " |
| | | | | | | | 50 | 2.07 | -1 | 0.48 | 10.0 | | | | " |
| .18 | $C_2H_5COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | $G^*$ | 25 | 1.01 | -2 | | | | | | (3) |
| .19 | $C_2H_5COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 4.47 | -6 | - | 15.0 (75 - 153°) | 2.9 | 3 | * | (1) |
| .20 | $C_2H_5COOH + (CH_3)_2CHCH_2OH$ | B | 0.1 | HCl | 0.1 | $G^*$ | 25 | 8.81 | -4 | 0.089 | | | | * | (5) |
| .21 | $C_2H_5COOH + cyclo\text{-}C_6H_{11}OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 2.24 | -6 | - | 16.5 (100 - 154°) | 1.7 | 4 | * | (1) |
| .22 | $C_3H_7COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | $G^*$ | 20 | 2.11 | -2 | 0.20 | | | | * | (14) |
| | | | | | | | 25 | 2.90 | -2 | 0.22 | | | | | " |
| | | | | | | | 30 | 3.72 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 6.52 | -2 | 0.32 | | | | | " |
| | | | | | | | 50 | 1.03 | -1 | 0.42 | 10.0 | 5.7 | 5 | | " |
| | | B | 0.1 | HCl | 0.002 - 0.006 | | 20 | (2.28) | -2 | 0.16 | (11.8) (75 - 150°) | 1.5 | 7 | | (1) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .22 | $C_3H_7COOH + CH_3OH$ *(continued)* | B | 0.1 | HCl | 0.005 | G* | 20 | 2.15 | -2 | 0.20 | | | | * | (17) |
| | | | | | | | 30 | 3.81 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 6.70 | -2 | 0.34 | | | | | " |
| | | | | | | | 50 | 1.08 | -1 | 0.48 | 10.0 | | | | " |
| | | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.05 | | 25 | 2.86 | -2 | 0.21 | | | | * | (2) |
| | | 1 | | | | | 25 | 4.54 | -3 | " | | | | | |
| | | 2 | | | | | 25 | 2.20 | -3 | " | | | | | |
| .23 | $C_3H_7COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 5.30 | -3 | | | | | | (3) |
| .24 | $C_3H_7COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 3.0 | -6 | - | 14.8 | 1.5 | 3 | * | (1) |
| | | | | | | | | | | | (75 - 154°) | | | | |
| .25 | $C_3H_7COOH + C_3H_7OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 - 0.1 | | HCl | 0.1 | | 25 | 8.82 | -4 | 0.11 | | | | * | (6) |
| .26 | $C_3H_7COOH + (CH_3)_2CHCH_2OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 3.98 | -3 | 0.089 | | | | * | (5) |
| | | 0.2 | | | | | " | 4.47 | -3 | | | | | | |
| | | 2.0 | | | | | " | 6.08 | -3 | | | | | | |
| .27 | $C_3H_7COOH$ + *cyclo*-$C_6H_{11}OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 1.59 | -6 | - | 15.7 | 2.7 | 3 | * | (1) |
| | | | | | | | | | | | (100 - 154°) | | | | |
| .28 | $(CH_3)_2CHCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 1.47 | -2 | 0.18 | | | | * | (15) |
| | | | | | | | 30 | 2.63 | -2 | 0.23 | | | | | " |
| | | | | | | | 40 | 4.40 | -2 | 0.30 | | | | | " |
| | | | | | | | 50 | 7.27 | -2 | 0.42 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $\tau$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .28 | $(CH_3)_2CHCOOH + CH_3OH$ *(continued)* | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.05 | | 25 | 1.98 | -2 | 0.21 | | | | * | (2) |
| | | 1 | | | | | " | 3.36 | -3 | " | | | | | " |
| | | 2 | | | | | " | 1.72 | -3 | " | | | | | " |
| .29 | $(CH_3)_2CHCOOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 4.04 | -3 | | | | | | (3) |
| .30 | $(CH_3)_2CHCOOH + (CH_3)_2CHCH_2OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 2.60 | -4 | 0.089 | | | | * | (5) |
| | | 1.0 | | | | | " | 2.81 | -4 | " | | | | | |
| | | 2.0 | | | | | " | 3.31 | -4 | " | | | | | |
| .31 | $C_4H_9COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.14 | -2 | 0.18 | | | | * | (14) |
| | | | | | | | 25 | 3.08 | -2 | 0.21 | | | | | " |
| | | | | | | | 30 | 4.02 | -2 | 0.23 | | | | | " |
| | | | | | | | 40 | 6.55 | -2 | 0.30 | | | | | " |
| | | | | | | | 50 | 1.03 | -1 | 0.42 | 10.0 | 5.7 | 5 | | " |
| | | B | 0.1 | HCl | 0.005 | G* | 20 | 2.25 | -2 | 0.20 | | | | | (17) |
| | | | | | | | 30 | 4.15 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 7.12 | -2 | 0.34 | | | | | " |
| | | | | | | | 50 | 1.14 | -1 | 0.48 | 10.2 | | | | " |
| .32 | $C_4H_9COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 5.07 | -3 | | | | | | (3) |
| .33 | $(CH_3)_2CHCH_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 4.88 | -3 | 0.18 | | | | * | (15) |
| | | | | | | | 30 | 8.77 | -3 | 0.23 | | | | | " |
| | | | | | | | 40 | 1.54 | -2 | 0.30 | | | | | " |
| | | | | | | | 50 | 2.48 | -2 | 0.42 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .33 | $(CH_3)_2CHCH_2COOH + CH_3OH$ *(continued)* | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.05 | | 25 | 7.45 | -3 | 0.21 | | | | * | (2) |
| | | 1 | | | | | " | 1.25 | -3 | " | | | | | " |
| | | 2 | | | | | " | 6.66 | -4 | " | | | | | " |
| .34 | $(CH_3)_2CHCH_2COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 1.21 | -3 | | | | | | (3) |
| .35 | $(CH_3)_2CHCH_2COOH + C_3H_7OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 1.77 | -4 | 0.11 | | | | * | (6) |
| | | 1.0 | | | | | " | 2.17 | -4 | " | | | | | " |
| | | 2.0 | | | | | " | 2.28 | -4 | " | | | | | " |
| .36 | $(CH_3)_2CHCH_2COOH + (CH_3)_2CHCH_2OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 7.17 | -5 | 0.089 | | | | * | (5) |
| | | 1.0 | | | " | | " | 1.24 | -4 | " | | | | | |
| | | 2.0 | | | " | | " | 1.43 | -4 | " | | | | | |
| .37 | $C_2H_5CH(CH_3)COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 4.05 | -3 | 0.18 | | | | * | (15) |
| | | | | | | | 30 | 7.20 | -3 | 0.23 | | | | | " |
| | | | | | | | 40 | 1.31 | -2 | 0.30 | | | | | " |
| | | | | | | | 50 | 2.19 | -1 | 0.42 | | | | | " |
| .38 | $(CH_3)_3CCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 1.40 | -3 | | | | | * | (16) |
| | | | | | | | 30 | 2.68 | -3 | | | | | | " |
| | | | | | | | 40 | 4.93 | -3 | | | | | | " |
| | | | | | | | 50 | 8.58 | -3 | | 11.4 | | | | " |
| .39 | $(CH_3)_3CCOOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 2.44 | -5 | | | | | | (3) |

942151 O—51——7

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .40 | $C_5H_{11}COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | $G^*$ | 20 | 2.19 | -2 | 0.18 | | | | * | (14) |
| | | | | | | | 30 | 3.91 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 6.54 | -2 | 0.30 | | | | | " |
| | | | | | | | 50 | 1.02 | -1 | 0.42 | 10.0 | 5.7 | 5 | | " |
| | | B | 0.1 | HCl | 0.002 - 0.006 | | 20 | (2.08) | -2 | 0.14 | (11.7) | (1.1) | 6 | * | (1) |
| | | | | | | | | | | | (75 - 154°) | | | | |
| | | B | 0.1 | HCl | 0.005 | $G^*$ | 20 | 2.42 | -2 | 0.20 | | | | * | (17) |
| | | | | | | | 30 | 4.26 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 7.19 | -2 | 0.34 | | | | | " |
| | | | | | | | 50 | 1.17 | -1 | 0.48 | 9.9 | | | | " |
| .41 | $C_5H_{11}COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 3.38 | -6 | - | 15.1 | 2.57 | 3 | * | (1) |
| | | | | | | | | | | | (75 - 154°) | | | | |
| .42 | $C_5H_{11}COOH$ + *cyclo*-$C_6H_{11}OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 1.89 | -6 | - | 15 | 1.25 | 2 | * | (1) |
| | | | | | | | | | | | (100 - 154°) | | | | |
| .43 | $(CH_3)_2CH(CH_2)_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | $G^*$ | 20 | 2.24 | -2 | | | | | * | (15) |
| | | | | | | | 30 | 3.83 | -2 | | | | | | |
| | | | | | | | 40 | 6.34 | -2 | | | | | | |
| | | | | | | | 50 | 1.04 | -1 | | | | | | |
| .44 | $C_2H_5CH(CH_3)CH_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | $G^*$ | 20 | 4.63 | -3 | | | | | * | (16) |
| | | | | | | | 30 | 8.05 | -3 | | | | | | " |
| | | | | | | | 40 | 1.43 | -2 | | | | | | " |
| | | | | | | | 50 | 2.40 | -2 | | 10.4 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .45 | $(C_2H_5)_2CHCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 3.51 | -4 | | | | | * | (16) |
| | | | | | | | 30 | 7.11 | -4 | | | | | | " |
| | | | | | | | 40 | 1.32 | -3 | | | | | | " |
| | | | | | | | 50 | 2.53 | -3 | | 12.4 | | | | " |
| .46 | $C_6H_{13}COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.11 | -2 | 0.11 | | | | * | (14) |
| | | | | | | | 30 | 3.80 | -2 | 0.20 | | | | | " |
| | | | | | | | 40 | 6.52 | -2 | 0.25 | | | | | " |
| | | | | | | | 50 | 1.00 | -1 | 0.42 | 10.0 | 5.7 | 5 | | " |
| | | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.05 | | 25 | 2.88 | -2 | 0.21 | | | | * | (2) |
| | | 1 | | | | | " | 4.88 | -3 | " | | | | | " |
| | | 2 | | | | | " | 2.48 | -3 | " | | | | | " |
| .47 | $C_6H_{13}COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 5.11 | -3 | | | | | | (3) |
| .48 | $C_6H_{13}COOH + (CH_3)_2CHCH_2OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | * | |
| | | 0 | | HCl | 0.1 | | 25 | 4.03 | -4 | 0.089 | | | | * | (5) |
| | | 1.0 | | | " | | " | 4.96 | -4 | " | | | | | |
| | | 2.0 | | | " | | " | 5.82 | -4 | " | | | | | |
| .49 | $(C_3H_7)_2CHCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.97 | -4 | | | | | * | (16) |
| | | | | | | | 30 | 6.31 | -4 | | | | | | " |
| | | | | | | | 40 | 1.22 | -3 | | | | | | " |
| | | | | | | | 50 | 2.27 | -3 | | 12.4 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $r$ | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k$ | $n$ | | | $A^o$ | $n$ | | |
| .50 | $C_8H_{17}COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.1 | -2 | 0.11 | | | | * | (14) |
| | | | | | | | 40 | 6.5 | -2 | 0.25 | 10.0 | 5.7 | 5 | | " |
| | | B | 0.1 | HCl | 0.002 - 0.006 | | 20 | (1.98) | -2 | 0.39 | (11.3) (0 - 45°) | (1.56) | 6 | * | (1) |
| .51 | $C_8H_{17}COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 3.8 | -6 | - | 14.9 (75 - 153°) | 2.19 | 3 | * | (1) |
| .52 | $C_8H_{17}COOH$ + *cyclo*-$C_6H_{11}OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 1.9 | -6 | - | 15.4 (100 - 153°) | 2.16 | 3 | * | (1) |
| .53 | $(C_4H_9)_2CHCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.67 | -4 | | | | | * | (16) |
| | | | | | | | 30 | 5.53 | -4 | | | | | | " |
| | | | | | | | 40 | 1.10 | -3 | | | | | | " |
| | | | | | | | 50 | 2.07 | -3 | | 12.9 | | | | " |
| .54 | $[(CH_3)_2CHCH_2]_2CHCOOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 1.40 | -4 | | | | | * | (16) |
| | | | | | | | 30 | 2.80 | -4 | | | | | | " |
| | | | | | | | 40 | 5.47 | -4 | | | | | | " |
| | | | | | | | 50 | 1.05 | -3 | | 12.6 | | | | " |
| .55 | $C_{11}H_{23}COOH + CH_3OH$ | B | 0.1 | HCl | 0.005 | G* | 20 | 2.23 | -2 | 0.20 | | | | * | (17) |
| | | | | | | | 30 | 4.04 | -2 | 0.25 | | | | | " |
| | | | | | | | 40 | 6.89 | -2 | 0.34 | | | | | " |
| | | | | | | | 50 | 1.13 | -1 | 0.48 | 10.2 | | | | " |
| | | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.05 | | 25 | 2.88 | -2 | 0.21 | | | | * | (2) |
| | | 1 | | | | | " | 4.70 | -3 | " | | | | | " |
| | | 2 | | | | | " | 2.39 | -3 | " | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .56 | $C_{11}H_{23}COOH + (CH_3)_2CHCH_2OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.1 | | 25 | 3.84 | -4 | 0.089 | | | | * | (5) |
| | | 1.0 | | | " | | " | 4.74 | -4 | " | | | | | " |
| .57 | $C_{15}H_{31}COOH + CH_3OH$ | B | 0.1 | HCl | 0.002 - 0.006 | G* | 20 | 2.2 | -12 | 0.13 | 11.8 (0 - 45°) | 1.5 | 7 | * | (1) |
| .58 | $C_{15}H_{31}COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 4.27 | -6 | - | 15.1 (75 - 154°) | 3.2 | 3 | * | (1) |
| .59 | $C_{15}H_{31}COOH$ + *cyclo*-$C_6H_{11}OH$ | B | 0.5 | - | - | $kA^2$ | 100 | 2.09 | -6 | - | 15.4 (100 - 154°) | 2.4 | 3 | * | (1) |
| .60 | $C_{21}H_{43}COOH + C_2H_5OH$ | B | 1.0 | - | - | $kA^2$ | 100 | 4.3 | -6 | - | 15.1 (75 - 154°) | 3.2 | 3 | * | (1) |
| .61 | $C_{21}H_{43}COOH$ + *cyclo*-$C_6H_{11}OH$ | B | 0.08 | - | - | $kA^2$ | 100 | 2.49 | -6 | - | 14.3 (100 - 154°) | 6.3 | 2 | * | (1) |
| | **Aryl - substituted aliphatic acid** | | | | | | | | | | | | | | |
| .62 | $C_6H_5CH_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 1.97 | -2 | | | | | * | (15) |
| | | | | | | | 25 | 2.62 | -2 | | | | | | " |
| | | | | | | | 30 | 3.44 | -2 | | | | | | " |
| | | | | | | | 40 | 5.84 | -2 | | | | | | " |
| | | | | | | | 50 | 9.44 | -2 | | 9.9 | | | | " |
| | | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.05 | | 25 | 2.85 | -2 | 0.21 | | | | * | (2) |
| | | 1 | | | | | " | 4.97 | -3 | " | | | | | |
| | | 2 | | | | | " | 2.39 | -3 | " | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .63 | $C_6H_5CH_2COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.05 | G* | 25 | 6.02 | -3 | | | | | | (3) |
| .64 | $C_6H_5CH_2COOH + C_3H_7OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | | HCl | 0.01 | | 25 | 7.18 | -4 | 0.055 | | | | * | (6) |
| | | 0 | | | 0.1 | | " | 1.23 | -3 | 0.11 | | | | | " |
| | | 0.1 | | | " | | " | 1.23 | -3 | " | | | | | " |
| | | 0.5 | | | " | | " | 1.06 | -3 | " | | | | | " |
| | | 2.0 | | | " | | " | 1.01 | -3 | " | | | | | " |
| | | 0 | " | HBr | 0.01 | " | " | 7.72 | -4 | 0.055 | | | | * | " |
| | | 0 | | | 0.1 | | " | 1.51 | -3 | 0.11 | | | | | " |
| | | 0.1 | | | " | | " | 1.51 | -3 | " | | | | | " |
| | | 0.5 | | | " | | " | 1.06 | -3 | " | | | | | " |
| | | 2.0 | | | " | | " | 9.92 | -4 | " | | | | | " |
| | | 0.1 | " | HI | 0.1 | " | " | 1.40 | -3 | 0.11 | | | | | " |
| .65 | $C_6H_5CH_2COOH + C_4H_9OH$ | B + $H_2O$(M/l) | 0.1 | | | G* | | | | | | | | | |
| | | 0 | " | HCl | 0.1 | | 25 | 4.20 | -4 | 0.12 | | | | | (4) |
| | | 0.1 | " | | " | | " | 2.24 | -4 | " | | | | | " |
| | | 0.2 | " | | " | | " | 1.43 | -4 | " | | | | | " |
| | | 1.0 | " | | " | | " | 4.00 | -4 | " | | | | | " |
| | | 0 | " | HBr | 0.1 | " | 25 | 4.72 | -4 | " | | | | | " |
| | | 0 | " | HI | 0.1 | " | 25 | 4.78 | -4 | " | | | | | " |
| .66 | $C_6H_5CH_2COOH + (CH_3)_2CHCH_2OH$ | B | 0.1 | HCl | 0.005 | G* | 25 | 2.49 | -4 | 0.035 | | | | * | (5) |
| | | | | | 0.01 | | " | 2.74 | -4 | 0.04 | | | | | " |
| | | | | | 0.05 | | " | 4.17 | -4 | 0.06 | | | | | " |
| | | | | | 0.1 | | " | 6.01 | -4 | 0.089 | | | | | " |

202.441.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .66 | $C_6H_5CH_2COOH + (CH_3)_2CHCH_2OH$ *(continued)* | B | 0.1 | HBr | 0.1 | G* | 25 | 3.27 | -4 | 0.089 | | | | * | (5) |
| | | " | " | HI | " | " | " | 3.32 | -4 | " | | | | | " |
| | | B + $H_2O$(M/l) | " | | | | | | | | | | | | |
| | | 0 | | HCl | 0.1 | " | " | 6.01 | -4 | 0.089 | | | | * | (5) |
| | | 0.2 | | | " | | " | 6.20 | -4 | " | | | | | " |
| | | 2.0 | | | " | | " | 7.34 | -4 | " | | | | | " |
| | | B | | $(NO_2)_2C_6H_2OH$ | 0.01 | " | " | 1.26 | -4 | 0.25 | | | | * | (5) |
| | | | 0.1 | | 0.02 | | " | 1.03 | -4 | " | | | | | " |
| .67 | $C_6H_5CH(C_2H_5)COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 1.33 | -3 | | | | | * | (18) |
| | | | | | | | 30 | 2.45 | -3 | | | | | | " |
| | | | | | | | 40 | 4.46 | -3 | | | | | | " |
| | | | | | | | 50 | 7.78 | -3 | | 11.1 | | | | " |
| | | " | 0.1 | HCl | 0.005 | G* | 0 | 3.63 | -4 | | | | | * | (9) |
| | | | | | | | 24 | 1.90 | -3 | | | | | | " |
| | | | | | | | 34 | 3.36 | -3 | | | | | | " |
| | | | | | | | 44 | 5.54 | -3 | | | | | | " |
| | | | | | | | 54 | 1.07 | -2 | | | | | | " |
| | | | | | | | 100 | 7.80 | -2 | | 10.8 | 1.8 | 5 | | " |
| .68 | $(C_6H_5)_2CHCOOH + C_6H_5CH_2OH$ | B | 0.1 | - | - | $kA^2$ | 100 | 2.10 | -6 | | | | | * | (9) |
| | | | | | | | 119 | 6.73 | -6 | | | | | | " |
| | | | | | | | 140 | 1.81 | -5 | | | | | | " |
| | | | | | | | 155 | 3.80 | -5 | | | | | | " |
| | | | | | | | 163 | 1.08 | -4 | | 16.3 | 8.9 | 3 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $r$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .69 | $C_6H_5(CH_2)_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.00 | -2 | | | | | * | ([15]) |
| | | | | | | | 25 | 2.67 | -2 | | | | | | " |
| | | | | | | | 30 | 3.56 | -2 | | | | | | " |
| | | | | | | | 40 | 5.89 | -2 | | | | | | " |
| | | | | | | | 50 | 9.20 | -2 | | 10.1 | | | | " |
| .70 | $C_6H_5(CH_2)_2COOH + C_2H_5OH$ | B | 0.1 | HCl | 0.005 | G* | 25 | 6.34 | -3 | | | | | | ([3]) |
| .71 | $C_6H_5(CH_2)_3COOH + CH_3OH$ | B | | HCl | 0.005 | G* | 20 | 2.01 | -2 | | | | | * | ([15]) |
| | | | | | | | 25 | 2.67 | -2 | | | | | | " |
| | | | | | | | 30 | 3.52 | -2 | | | | | | " |
| | | | | | | | 40 | 6.08 | -2 | | | | | | " |
| | | | | | | | 50 | 1.00 | -1 | | 9.6 | | | | " |
| | **Cycloalkyl - substituted aliphatic acid** | | | | | | | | | | | | | | |
| .72 | *cyclo*-$C_6H_{11}CH_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 5.25 | -3 | | | | | * | ([18]) |
| | | | | | | | 30 | 9.79 | -3 | | | | | | " |
| | | | | | | | 40 | 1.70 | -2 | | | | | | " |
| | | | | | | | 50 | 2.79 | -2 | | 10.5 | | | | " |
| .73 | *cyclo*-$C_6H_{11}(CH_2)_2COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 2.10 | -2 | | | | | * | ([18]) |
| | | | | | | | 30 | 3.54 | -2 | | | | | | " |
| | | | | | | | 40 | 5.98 | -2 | | | | | | " |
| | | | | | | | 50 | 1.06 | -1 | | 10.1 | | | | " |
| .74 | *cyclo*-$C_6H_{11}(CH_2)_3COOH + CH_3OH$ | B | 0.5 | HCl | 0.005 | G* | 20 | 1.94 | -2 | | | | | * | ([18]) |
| | | | | | | | 30 | 3.28 | -2 | | | | | | " |
| | | | | | | | 40 | 5.74 | -2 | | | | | | " |
| | | | | | | | 50 | 9.56 | -2 | | 10.1 | | | | " |

## SUPPLEMENTARY TABLES

Effect of pressure ([12])

(.5) $CH_3COOH + C_2H_5OH$

| °C | $10^7 k$ | | | | $E$ | $A$ |
|---|---|---|---|---|---|---|
| P (atm) | 50 | 60 | 70 | 75 | | |
| 1 | 2.34 | 4.20 | 7.98 | 12.7 | 13.77 | $4.58 \times 10^2$ |
| 2000 | 12.35 | 20.88 | 41.42 | 58.10 | 13.79 | $2.40 \times 10^2$ |
| 3000 | 25.63 | 47.92 | 81.30 | 125.10 | 13.83 | $6.10 \times 10^3$ |
| 3750 | - | - | - | 227.5 | - | - |
| 4000 | 60.01 | 101.35 | 193.80 | - | 13.98 | $1.61 \times 10^4$ |

(.8) $CH_3COOH + n\text{-}C_4H_9OH$

| °C | $10^7 k$ | | | $E$ | $A$ |
|---|---|---|---|---|---|
| P (atm) | 70 | 75 | 80 | | |
| 1 | 10.41 | 13.07 | 17.27 | 13.7 | $5.69 \times 10^2$ |
| 2000 | 32.20 | 51.88 | 73.70 | 14.58 | $7.0 \times 10^3$ |
| 3000 | 74.20 | 100.40 | 145.20 | 14.95 | $2.4 \times 10^4$ |
| 3750 | 123.0 | 167.0 | 226.0 | 15.19 | $5.72 \times 10^4$ |

## SUPPLEMENTARY TABLES *(continued)*

(.10) $CH_3COOH + (C_2H_5)(CH_3)CHOH$

| °C | $10^7 k$ | | | | |
|---|---|---|---|---|---|
| p (atm) | 70 | 75 | 80 | $E$ | $A$ |
| 1 | 1.77 | 2.63 | 3.89 | 17.5 | $2.5 \times 10^4$ |
| 2000 | 9.68 | 14.13 | 21.14 | 19.8 | $3.5 \times 10^6$ |
| 3000 | 20.65 | 31.75 | 49.20 | 21.0 | $4.9 \times 10^7$ |
| 3750 | 30.22 | 57.60 | 90.50 | 21.7 | $2.2 \times 10^8$ |

**General.** (G*) The Goldschmidt equation, $kA[H^+]r/(M + r)$, $r = [BH^+][M]/[MH^+]$, integrated form

$$k = \frac{1}{t[H^+]} \left[(a + r) \ln \frac{ar}{a - x} - x\right],$$

accounts for the gradual decrease of the concentration of the catalytically active $BH^+$ with the progress of the esterification, through its increasing replacement by the less active $MH^+$. The empirical values of the parameter $r$, used for calculation, are included beside $k$ whenever they are stated. The catalytic effect of the acid HX, assumed to be composed of the effect of $BH^+$ and of B.HX, was expressed by Goldschmidt ([2,3]), by representation of $k$ as the sum of two terms, $k = k_{BH^+}\ \gamma + k_{BHX}\ (1 - \gamma)$, and the two constants given separately; these data were not included in these tables. For weak acids, at the concentration $c$, the ratio $k/c\alpha$, where $\alpha$ = degree of dissociation, is fairly constant, thus, for reactions (.2) and (.62) in catalysis by $(NO_2)_3C_6H_2OH$, $(NO_2)_3 - m\text{-}C_6H(OH)CH_3$, $CCl_3COOH$ ([7]), and catalysis by $(NO_2)_3 - m\text{-}C_6H(OH)CH_3$ of the reactions (.4), (.23), (.33), (.62) ([8]).

**Data of Goldschmidt et al.** ([2]) to ([8]), were recalculated from hour to sec. On the basis of comparisons particularly with data of H.A.Smith et al. ([14]) to ([18]), it appears certain that the data of ([2]) to ([8]) have been calculated with decimal logarithms. Consequently, all $k$ values of ([2]) to ([8]) were multiplied by 2.303; thus converted to ln, data of ([2]) to ([8]) check fairly well, at times very well with those of ([14]) to ([18]) which are rated highly reliable. The two sets of data are, thus, satisfactorily comparable and mutually complementary for reactions covered only by one of the two sets.

Data of ([2]) to ([8]) and those of ([14]) to ([18]) even though close, are tabulated separately. Data of the H. A. Smith and the Hinshelwood schools have been amalgamated whenever possible; *very close* data from different sources have been averaged and are underlined.

**Uncatalyzed esterification.** In the absence of a catalyzing acid, ([9]) finds the law $kA^2$ to be valid. It accounts for the catalytic action of A itself.

**Order of reactions.** The reactions are arranged by acids, by increasing numbers of C atoms, and subdivided into purely aliphatic, aryl-substituted and cycloalkyl-substituted acids. Bulk formulae of alkyls refer to the normal unbranched structure. Branched acids follow, in the order of increasing branching, the normal acids. Under each acid, the reactions are ordered by the alcohols, on the same principle. Acid-catalyzed and uncatalyzed reactions are numbered separately.

# LITERATURE

(1) R.A.Fairclough, C.N.Hinshelwood, *CSL* **1939**, 593. (2) H.Goldschmidt, A.Thuesen, *ZPC* 1913, **81**, 30. (3) H.Goldschmidt et al., ZPC 1920, **94**, 233. (4) H.Goldschmidt, E.Mathiesen, *ZPC* 1926, **121**, 153. (5) H.A.Goldschmidt et al., *ZPC* 1926, **124**, 23. (6) H.Goldschmidt, L.Thomas, *ZPC* 1927, **126**, 24. (7) H.Goldschmidt, E.Marum, L.Thomas, *ZPC* 1927, **129**, 223. (8) H.Goldschmidt, E.Marum, L.Thomas, *ZPC* 1928, **132**, 257. (9) C.N.Hinshelwood, A.R.Legard, *CSL* **1935**, 587.

(10) E.A.Moelwyn-Hughes, C.N.Hinshelwood, *CSL* **1932**, 230. (11) E.A.Moelwyn-Hughes, A.C.Rolfe, *CSL* **1932**, 241. (12) S.Peng, R.N.Sapiro, R.P.Linstead, D.M.Newitt, *CSL* **1938**, 784. (13) A.C.Rolfe, C.N.Hinshelwood, *TFS* 1934, **30**, 935. (14) H.A.Smith, *ACS* 1939, **61**, 254. (15) H.A.Smith, *ACS* 1939, **61**, 1176. (16) H.A.Smith, *ACS* 1940, **62**, 1136. (17) H.A.Smith, C.H.Reichardt, *ACS* 1941, **63**, 605. (18) H. A. Smith, J. Burn, *ACS* 1944, **66**, 1494. (19) A.T.Williamson, C.N.Hinshelwood, *TFS* 1934, **30**, 1145.

# ESTERIFICATION

## Aromatic carboxylic acid + Alcohol

Reaction type $\underset{(A)}{ArCOOH} + \underset{(B)}{R'OH} \rightarrow \underset{(L)}{ArCOOR'} + \underset{(M)}{H_2O}$

Rate measured $-dA/dt = +dL/dt$

G* = Goldschmidt equation, $kA[H^+]r/(M + r)$ $r = [BH^+][M]/[MH^+]$

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.
Comments, Literature, at the end of the table.

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5COOH + CH_3OH$ | B | | HCl | G* | 25 | 1.92 | -4 | | | | * | ([3]) |
| | | | | 0.02 - 0.1 | | 40 | 6.52 | -4 | | | | | " |
| | | | | | | 60 | 2.93 | -3 | 15.5 | | | | " |
| | | " | 0.1 | " | " | 0 | 1.67 | -5 | | | | * | ([5]) |
| | | | | 0.002 - 0.006 | | 25 | 1.92 | -4 | | | | | " |
| | | | | | | 40 | 6.53 | -4 | | | | | " |
| | | | | | | 51 | 1.55 | -3 | | | | | " |
| | | | | | | 63 | 3.03 | -3 | | | | | " |
| | | | | | | 100 | 4.0 | -2 | 15.7 | 6.0 | 7 | | " |
| | | " | 1.0 | | $kA^2$ | 100 | 5.11 | -7 | | | | | " |
| | | | | | | 120 | 1.71 | -6 | | | | | " |
| | | | | | | 139 | 5.61 | -6 | | | | | " |
| | | | | | | 153 | 1.11 | -5 | 18.3 | 3.0 | 4 | | " |
| .2 | $C_6H_5COOH + CH_3OH$ | B + $H_2O$(M/l) | 0.1 | | G* | | | | | | | | ([2a]) |
| | | 0 | | HCl 0.05 | | 25 | 8.65 | -5 | 0.21 | | | | |
| | | 1 | | | | " | 1.24 | -5 | " | | | | |
| | | 2 | | | | " | 5.5 | -6 | " | | | | |
| .3 | $C_6H_5COOH + (CH_3)_2CHOH$ | B | 1.0 | | $kA^2$ | 100 | 5.3 | -8 | | | | * | ([5]) |
| | | | | | | 139 | 8.49 | -7 | | | | | |

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .3 | $C_6H_5COOH + (CH_3)_2CHOH$ (*continued*) | B | 1.0 | | $kA^2$ | 153 | 1.70 | −6 | | | | | (5) |
| | | | | | | 183 | 9.12 | −6 | | | | | " |
| | | | | | | 211 | 4.04 | −5 | 21.1 | 1.3 | 5 | | " |
| .4 | $C_6H_5COOH + (CH_3)_3COH$ | B | 1.0 | | $kA^2$ | 100 | 1.71 | −10 | | | | * | (5) |
| | | | | | | 183 | 1.49 | −7 | | | | | " |
| | | | | | | 194 | 3.10 | −7 | | | | | " |
| | | | | | | 211 | 8.85 | −7 | 27.5 | 2.3 | 6 | | " |
| .5 | $C_6H_5COOH + cyclo - C_6H_{11}OH$ | B | 0.1 | HCl | G* | 55 | 1.56 | −5 | | | | * | (4) |
| | | | | 0.02 − 0.1 | | 65 | 4.26 | −5 | | | | | " |
| | | | | | | 75 | 9.08 | −5 | | | | | " |
| | | | | | | 85 | 1.97 | −4 | 19.5 | 1.7 | 8 | | " |
| .6 | $C_6H_5COOH + C_6H_5CH_2OH$ | B | 1.0 | | $kA^2$ | 100 | 4.2 | −7 | | | | * | (5) |
| | | | | | | 121 | 1.71 | −6 | | | | | " |
| | | | | | | 139 | 5.46 | −6 | | | | | " |
| | | | | | | 154 | 1.19 | −5 | 19.7 | 1.8 | 5 | | " |
| | | $C_6H_6$ | | $p - CH_3C_6H_4SO_3H$ | $kAB$ | | | | | | | * | (1) |
| | | $A_o$ = | $B_o$ = | | | | | | | | | | |
| | | 0.2 | 0.1 | 0.01 | | 100 | 6.0 | −5 | | | | | |
| | | 0.1 | 0.2 | " | | " | 5.0 | −5 | | | | | |
| | | " | 0.1 | 0.02 | | " | 1.67 | −4 | | | | | |
| | | " | " | 0.01 | | 74.3 | 2.1 | −5 | | | | | |
| | | " | " | " | | 100 | 6.9 | −5 | | | | | |
| | | " | " | " | | 137 | 2.27 | −4 | | | | | |
| | | " | " | 0.002 | | 100 | 3.3 | −5 | | | | | |
| | | " | 0.01 | 0.005 | | " | 3.8 | −5 | | | | | |
| | | 0.01 | 0.1 | 0.002 | | " | 2.9 | −5 | | | | | |

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .7 | $o - CH_3C_6H_4COOH + CH_3OH$ | B | | HCl | G* | 25 | 5.41 | -5 | | | | * | (3) |
| | | | | 0.02 - 0.1 | | 40 | 2.02 | -4 | | | | | |
| | | | | | | 50 | 4.09 | -4 | | | | | |
| | | | | | | 60 | 8.14 | -4 | | | | | |
| .8 | $o - CH_3C_6H_4COOH + cyclo - C_6H_{11}OH$ | B | 0.1 | HCl | G* | 55 | 7.67 | -6 | | | | * | (4) |
| | | | | 0.02 - 0.1 | | 65 | 1.74 | -5 | | | | | " |
| | | | | | | 75 | 3.91 | -5 | | | | | " |
| | | | | | | 85 | 8.13 | -5 | 18.4 | 1.41 | 7 | | " |
| .9 | $m - CH_3C_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 2.17 | -4 | | | | * | (3) |
| | | | | | | 40 | 6.55 | -4 | | | | | " |
| | | | | | | 50 | 1.37 | -3 | | | | | " |
| | | | | | | 60 | 2.65 | -3 | 14.2 | | | | " |
| .10 | $p - CH_3C_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 1.94 | -4 | | | | * | (3) |
| | | | | | | 40 | 5.90 | -4 | | | | | " |
| | | | | | | 50 | 1.20 | -3 | | | | | " |
| | | | | | | 60 | 2.25 | -3 | 13.8 | | | | " |
| .11 | $2, 4, 6 - (CH_3)_3C_6H_2COOH + C_6H_4CH_2OH$ | B | 1.0 | | $kA^2$ | 100 | 7.41 | -10 | 27.7 | 1.45 | 7 | * | (5) |
| .12 | $o - CH_3OC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | HCl | G* | 55 | 5.23 | -5 | | | | * | (4) |
| | | | | 0.02 - 0.1 | | 65 | 1.26 | -4 | | | | | " |
| | | | | | | 75 | 2.53 | -4 | | | | | " |
| | | | | | | 85 | 5.61 | -4 | 18.2 | 7.52 | 7 | | " |
| .13 | $m - CH_3OC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 1.91 | -5 | | | | * | (4) |
| | | | | | | 65 | 5.04 | -5 | | | | | " |
| | | | | | | 75 | 1.00 | -4 | 19.3 | 1.4 | 8 | | " |
| | | | | | | 85 | 2.39 | -4 | | | | | " |

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .14 | $p - CH_3OC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | 0.1 | HCl | G* | 55 | 7.2 | −6 | | | | * | (4) |
| | | | | 0.02 − 0.1 | | 65 | 1.96 | −5 | | | | | " |
| | | | | | | 75 | 3.50 | −5 | | | | | " |
| | | | | | | 85 | 1.07 | −4 | 20.2 | 2.13 | 8 | | " |
| .15 | $o - C_2H_5OC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 4.62 | −5 | | | | * | (4) |
| | | | | | | 65 | 1.17 | −4 | | | | | " |
| | | | | | | 75 | 2.42 | −4 | | | | | " |
| | | | | | | 85 | 5.34 | −4 | 18.8 | 1.69 | 8 | | " |
| .16 | $m - C_2H_5OC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 1.89 | −5 | | | | * | (4) |
| | | | | | | 65 | 5.50 | −5 | | | | | " |
| | | | | | | 75 | 1.12 | −4 | | | | | " |
| | | | | | | 85 | 2.20 | −4 | 18.9 | 7.91 | 7 | | " |
| .17 | $p - C_2H_5OC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 9.0 | −6 | | | | * | (4) |
| | | | | | | 65 | 1.97 | −5 | | | | | " |
| | | | | | | 75 | 4.62 | −5 | | | | | " |
| | | | | | | 85 | 8.49 | −5 | 17.7 | 5.74 | 6 | | " |
| .18 | $o - NO_2C_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 5.46 | −6 | | | | * | (3) |
| | | | | | | 40 | 2.43 | −5 | | | | | " |
| | | | | | | 60 | 1.72 | −4 | 19.0 | | | | " |
| | | " | " | | $kA^2$ | 100 | 3.54 | −7 | 20.7 | 5.4 | 5 | * | (5) |
| .19 | $m - NO_2C_6H_4COOH + CH_3OH$ | B | " | " | G* | 25 | 7.28 | −5 | | | | * | (3) |
| | | | | | | 40 | 2.34 | −4 | | | | | " |
| | | | | | | 50 | 4.81 | −4 | | | | | " |
| | | | | | | 60 | 9.36 | −4 | 14.6 | | | | " |

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .20 | $p - NO_2C_6H_4COOH + CH_3OH$ | B | 0.1 | HCl | G* | 25 | 8.67 | -5 | | | | * | ([3]) |
| | | | | 0.02 - 0.1 | | 40 | 2.74 | -4 | | | | | " |
| | | | | | | 50 | 5.77 | -4 | | | | | " |
| | | | | | | 60 | 1.15 | -3 | 14.7 | | | | " |
| .21 | $3, 5 - (NO_2)_2C_6H_3COOH + CH_3OH$ | B | " | " | " | 30 | 3.33 | -5 | | | | * | ([2]) |
| | | | | | | 40 | 8.37 | -5 | | | | | " |
| | | | | | | 50 | 1.73 | -4 | | | | | " |
| | | | | | | 60 | 3.50 | -4 | 15.5 | | | | " |
| .22 | $o - FC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 2.35 | -5 | | | | * | ([4]) |
| | | | | | | 65 | 5.45 | -5 | | | | | " |
| | | | | | | 75 | 1.11 | -4 | | | | | " |
| | | | | | | 85 | 2.26 | -4 | 17.5 | 1.11 | 7 | | " |
| .23 | $m - FC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 2.21 | -5 | | | | * | ([4]) |
| | | | | | | 65 | 4.93 | -5 | | | | | " |
| | | | | | | 75 | 1.03 | -4 | | | | | " |
| | | | | | | 85 | 2.34 | -4 | 18.2 | 3.02 | 7 | | " |
| .24 | $p - FC_6H_4COOH + cyclo - C_6H_{11}OH$ | B | " | " | " | 55 | 1.48 | -5 | | | | * | ([4]) |
| | | | | | | 65 | 4.43 | -5 | | | | | " |
| | | | | | | 75 | 8.37 | -5 | | | | | " |
| | | | | | | 85 | 1.53 | -4 | 17.9 | 1.4 | 7 | | " |
| .25 | $o - ClC_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 7.83 | -5 | | | | * | ([3]) |
| | | | | | | 40 | 2.51 | -4 | | | | | " |
| | | | | | | 50 | 5.02 | -4 | | | | | " |
| | | | | | | 60 | 1.02 | -3 | 14.6 | | | | " |



942151 O—51——8

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | E | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .26 | $m - ClC_6H_4COOH + CH_3OH$ | B | 0.1 | HCl | G* | 25 | 1.24 | -4 | | | | * | ([3]) |
| | | | | 0.02 - 0.1 | | 40 | 3.83 | -4 | | | | | " |
| | | | | | | 50 | 8.04 | -4 | | | | | " |
| | | | | | | 60 | 1.57 | -3 | 14.6 | | | | " |
| .27 | $p - ClC_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 1.14 | -4 | | | | * | ([3]) |
| | | | | | | 40 | 3.66 | -4 | | | | | " |
| | | | | | | 50 | 7.66 | -4 | | | | | " |
| | | | | | | 60 | 1.54 | -3 | 14.6 | | | | " |
| .28 | $2, 4 - Cl_2C_6H_3COOH + CH_3OH$ | B | " | " | " | 30 | 4.58 | -5 | | | | * | ([2]) |
| | | | | | | 40 | 1.27 | -4 | | | | | " |
| | | | | | | 50 | 3.25 | -4 | | | | | " |
| | | | | | | 60 | 7.10 | -4 | 18.3 | | | | " |
| .29 | $2, 5 - Cl_2C_6H_3COOH + CH_3OH$ | B | " | " | " | 30 | 5.35 | -5 | | | | * | ([2]) |
| | | | | | | 40 | 1.17 | -4 | | | | | " |
| | | | | | | 50 | 2.36 | -4 | | | | | " |
| | | | | | | 60 | 4.75 | -4 | 14.5 | | | | " |
| .30 | $3, 5 - Cl_2C_6H_3COOH + CH_3OH$ | B | " | " | " | 30 | 9.08 | -5 | | | | * | ([2]) |
| | | | | | | 40 | 2.16 | -4 | | | | | " |
| | | | | | | 50 | 5.48 | -4 | | | | | " |
| | | | | | | 60 | 1.23 | -3 | 18.1 | | | | " |
| .31 | $o - BrC_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 5.55 | -5 | | | | * | ([3]) |
| | | | | | | 40 | 1.90 | -4 | | | | | " |
| | | | | | | 50 | 3.87 | -4 | 15.2 | | | | " |
| .32 | $m - BrC_6H_4COOH + CH_3OH$ | B | " | " | " | 25 | 1.25 | -4 | | | | * | ([3]) |
| | | | | | | 40 | 4.02 | -4 | | | | | " |

| No. | Reaction | Medium | Amount of reactant | Addend (Catalyst) | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .32 | *m* - $BrC_6H_4COOH + CH_3OH$ (*continued*) | B | 0.1 | HCl | O* | 50 | 8.25 | -4 | | | | | ([3]) |
| | | | | 0.02 - 0.1 | | 60 | 1.57 | -3 | 14.4 | | | | " |
| .33 | *p* - $BrC_6H_4COOH + CH_3OH$ | " | " | " | " | 25 | 1.23 | -4 | | | | * | ([3]) |
| | | | | | | 40 | 4.00 | -4 | | | | | " |
| | | | | | | 50 | 8.03 | -4 | 14.6 | | | | " |
| .34 | *o* - $IC_6H_4COOH$ + *cyclo* - $C_6H_{11}OH$ | B | " | " | " | 55 | 6.6 | -6 | | | | * | ([4]) |
| | | | | | | 65 | 1.87 | -5 | | | | | " |
| | | | | | | 75 | 3.40 | -5 | | | | | " |
| | | | | | | 85 | 6.68 | -5 | 17.6 | 4.12 | 6 | | " |
| .35 | *m* - $IC_6H_4COOH$ + *cyclo* - $C_6H_{11}OH$ | B | " | " | " | 55 | 3.16 | -5 | | | | * | ([4]) |
| | | | | | | 65 | 7.11 | -5 | | | | | " |
| | | | | | | 75 | 1.43 | -4 | | | | | " |
| | | | | | | 85 | 2.70 | -4 | 16.7 | 4.4 | 6 | | " |

## COMMENTS

**General.** (G*) The Goldschmidt equation, $kA[H^+]r/(M + r)$, $r = [BH^+][M]/[MH^+]$ accounts for the decrease of the concentration of the catalytically active $BH^+$ with the progress of the esterification, through its increasing replacement by the less active $MH^+$. The empirical values of the parameter $r$ used for the calculations of $k$ are given in the following. For the uncatalyzed esterification, without $H^+$ ions added in the form of HCl, ([5]) find a rate law $kA^2$, accounted for by a catalytic action of A itself. Values of $r$ used for the calculation of $k$:

| °C | 25 | 40 | 50 | 60 | ([3]) | 30 | 40 | 50 | 60 | ([2]) | 55 | 65 | 75 | 85 | ([4]) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $r$ | 0.22 | 0.36 | 0.50 | 0.65 | | 0.26 | 0.36 | 0.42 | 0.56 | | 0.60 | 0.30 | 0.25 | 0.20 | |
| | | | ($CH_3OH$) | | | | | ($CH_3OH$) | | | | | (*cyclo*-$C_6H_{11}OH$) | | |

(.6) The variation of $k$ with $A_o$ and $B_o$ in the data of ([1]) is ascribed to dimerization of both A and B and formation of AB complexes. The activation energy for the esterification (excluding association processes) is estimated to 3.5 kcal. (.8) (.12 - .17) (.22 - .24) (.26 - .27) $k$ valid between 20 % and 80 % conversion ([4]).

## LITERATURE

([1]) M.M.Davies, *TFS* 1937, 33, 331. ([2]) A.G.Gassman, R.J.Hartman, *ACS* 1941, 63, 2393. ([2a]) H.Goldschmidt et al., *ZPC* 1926, 124, 23. ([3]) R.J.Hartman, A.M.Borders, *ACS* 1937, 59, 2107. ([4]) R.J.Hartman, R.M.Hoogsteen, J. A. Moede, *ACS* 1944, 66, 1714. ([5]) C.N.Hinshelwood, A.R.Legard, *CSL* 1935, 587.

# ESTERIFICATION

## Aliphatic alcohol, Hydrohalic acid

*Liquid phase*

Reaction type $ROH + HX \rightarrow RX + H_2O$
(A) (B) (L) (M)

Rate law $-dB/dt = +dL/dt = kAB$

All rates are in M/l per sec.
All amounts in M/l.
Comments, Literature, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3OH + HBr$ | PhOH | A = 0.05; B = 0.1; M = 0.5 | 80 | 2.97 | -4 | | | (1) |
| | | | | 92 | 1.0 | -3 | 26.6 | | " |
| .2 | $C_2H_5OH + HBr$ | " | " | 80 | 5.29 | -5 | | | (1) |
| | | | | 92 | 2.20 | -4 | 31.3 | | " |
| .3 | $C_3H_7OH + HBr$ | " | " | 80 | 4.58 | -5 | | | (1) |
| | | | | 92 | 1.95 | -4 | 31.7 | | " |
| .4 | $C_4H_9OH + HBr$ | " | " | 80 | 4.70 | -5 | | | (1) |
| | | | | 92 | 1.83 | -4 | 29.6 | | " |
| .5 | $(CH_3)_2CHCH_2OH + HBr$ | " | " | 80 | 5.98 | -6 | | | (1) |
| | | | | 92 | 2.18 | -5 | 28.4 | | " |
| .6 | $(C_2H_5)(CH_3)CHOH + HBr$ | " | " | 80 | 2.89 | -4 | | | (1) |
| | | | | 92 | 1.13 | -3 | 29.9 | | " |
| .7 | $C_5H_{11}OH + HBr$ | " | " | 80 | 4.78 | -5 | | | (1) |
| | | | | 92 | 1.93 | -4 | 30.6 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .8 | $(CH_3)_2CHCH_2CH_2OH + HBr$ | PhOH | A = 0.05; B = 0.1; M = 0.5 | 80 | 1.21 | -4 | | | (1) |
| | | | | 92 | 4.82 | -4 | 30.1 | | " |
| .9 | $C_6H_{13}OH + HBr$ | " | " | 80 | 4.76 | -5 | | | (1) |
| | | | | 92 | 1.95 | -4 | 30.9 | | " |
| .10 | $C_7H_{15}OH + HBr$ | " | " | 80 | 4.87 | -5 | | | (1) |
| | | | | 92 | 1.93 | -4 | 30.1 | | " |
| .11 | $C_8H_{17}OH + HBr$ | " | " | 80 | 4.80 | -6 | | | (1) |
| | | | | 92 | 1.83 | -4 | 29.5 | | " |
| .12 | $C_{16}H_{33}OH + HBr$ | " | " | 80 | 4.80 | -5 | 26.6 | | (1) |
| | **Halogen-substituted Alcohol** | | | | | | | | |
| .13 | $CH_2ClCH_2OH + HBr$ | PhOH | A = 0.05; B = 0.1; M = 0.5 | 97 | 0 | | | | (1) |
| .14 | $CH_2Cl(CH_2)_2OH + HBr$ | " | " | 97 | 6.3 | -5 | 26.6 | | (1) |
| .15 | $CH_2Cl(CH_2)_3OH + HBr$ | " | " | 97 | 1.25 | -4 | 26.6 | | (1) |
| .16 | $CH_2Cl(CH_2)_6OH + HBr$ | " | " | 97 | 2.85 | -4 | 26.6 | | (1) |
| | **Aryl-substituted Alcohol** | | | | | | | | |
| .17 | $(C_6H_5)_2CHOH + HCl$ | $(CH_3)_2CO + H_2O$ 0.5556 | A = B = 0.1 | 50 | 1.83 | -4 | | * | (3) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .17 | $(C_6H_5)_2CHOH + HCl$ *(continued)* | $(CH_3)_2CO + H_2O$ | A = B = 0.1 | | | | | | |
| | | 1.1112 | | 50 | 1.54 | -4 | | | ([3]) |
| | | 2.7778 | | " | 3.53 | -5 | | | " |
| | | 5.5556 | | " | 5.18 | -6 | | | " |
| .18 | $(C_6H_5)_2CHOH$ / $(C_6H_5)_2CHOC_2H_5$ + HCl | $C_2H_5OH + H_2O$ % | $A_o = B_o = 0$; $L_o = 0.03 - 0.14$ | | | | | | |
| | | 0 | | 25 | 8.5 | -5 | | * | ([2]) |
| | | 0.15 | | " | 4.33 | -5 | | | " |
| | | 0.58 | | " | 2.00 | -5 | | | " |
| | | 1.07 | | " | 1.5 | -5 | | | " |
| | | 2.39 | | " | 2.5 | -5 | | | " |
| | | 7.19 | | " | 1.13 | -4 | | | " |
| .19 | $C_6H_5O(CH_2)_2OH + HBr$ | PhOH | A = 0.05; B = 0.1; M = 0.5 | 97 | 1.31 | -5 | 26.6 | | ([1]) |
| .20 | $o - CH_3C_6H_4O(CH_2)_2OH + HBr$ | " | " | 97 | 1.45 | -5 | 26.6 | | ([1]) |
| .21 | $m - CH_3C_6H_4O(CH_2)_2OH + HBr$ | " | " | 97 | 1.37 | -5 | 26.6 | | ([1]) |
| .22 | $p - CH_3C_6H_4O(CH_2)_2OH + Br$ | " | " | 97 | 1.67 | -5 | 25.5 | | ([1]) |
| .23 | $o - ClC_6H_4O(CH_2)_2OH + HBr$ | " | " | 97 | 9.3 | -5 | 26.6 | | ([1]) |
| .24 | $C_6H_5O(CH_2)_3OH + HBr$ | " | " | 86 | 4.62 | -5 | | | ([1]) |
| | | | | 97 | 1.57 | -4 | 24.3 | | " |
| .25 | $C_6H_5O(CH_2)_4OH + HBr$ | " | " | 86 | 1.82 | -4 | 25.8 | | ([1]) |
| | | | | 97 | 5.86 | -4 | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| | | | **Bialcohol** | | | | | | |
| .26 | $OH(CH_2)_2OH + HBr$ | PhOH | A = 0.05; B = 0.1; M = 0.5 | 76 | 1.5 | -6 | | | (1) |
| | | | | 85 | 5.08 | -5 | | | " |
| .27 | $OH(CH_2)_3OH + HBr$ | " | " | 76 | 6.84 | -5 | | | (1) |
| | | | | 85 | 3.12 | -4 | | | " |
| .28 | $OH(CH_2)_4OH + HBr$ | " | " | 76 | 4.55 | -4 | | | (1) |
| | | | | 85 | 2.24 | -3 | | | " |
| .29 | $OH(CH_2)_5OH + HBr$ | " | " | 76 | 3.95 | -4 | | | (1) |
| | | | | 85 | 1.05 | -3 | | | " |
| .30 | $OH(CH_2)_6OH + HBr$ | " | " | 76 | 2.18 | -4 | | | (1) |
| | | | | 85 | 5.9 | -4 | | | " |
| .31 | $OH(CH_2)_7OH + HBr$ | " | " | 76 | 2.00 | -4 | | | (1) |
| | | | | 85 | 6.41 | -4 | | | " |
| .32 | $OH(CH_2)_8OH + HBr$ | " | " | 76 | 2.48 | -4 | | | (1) |
| | | | | 85 | 5.14 | -4 | | | " |
| .33 | $OH(CH_2)_9OH + HBr$ | " | " | 76 | 2.56 | -4 | | | (1) |
| | | | | 85 | 6.19 | -4 | | | " |
| .34 | $OH(CH_2)_{10}OH + HBr$ | " | " | 76 | 2.30 | -4 | | | (1) |

## COMMENTS

Reverse reactions, see 212.471. (.17) Data not of high precision, owing to reaction between HCl and $(CH_3)_2CO$, resulting in a decrease of HCl; allowed for in the calculation of *k*. (.18) From reverse reaction.

## LITERATURE

(1) G. M. Bennett, F. M. Reynolds, *CSL* 1935, 131. (2) J. Norris, A. Morton, *ACS* 1928, **50**, 1795.
(3) W. Taylor, *ACS* 1938, **60**, 2094.

# ESTERIFICATION

## Polyalcohol and Hydrogen halide

*Liquid phase*

Amounts are in M/l.

Rates in M/l per sec.

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $HO(CH_2)_2OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 1.5 | -6 | |
| | | | | | 85.0 | 5.1 | -6 | 26.6 |
| .2 | $HO(CH_2)_3OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 6.8 | -6 | |
| | | | | | 85.0 | 3.1 | -5 | 26.6 |
| .3 | $HO(CH_2)_4OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 4.2 | -5 | |
| | | | | | 85.0 | 2.2 | -4 | 26.6 |
| .4 | $HO(CH_2)_5OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 3.9 | -5 | |
| | | | | | 85.0 | 1.0 | -4 | 26.6 |
| .5 | $HO(CH_2)_6OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 2.2 | -5 | |
| | | | | | 85.0 | 5.9 | -5 | 26.6 |
| .6 | $HO(CH_2)_7OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 2.0 | -5 | |
| | | | | | 85.0 | 6.4 | -5 | 26.6 |
| .7 | $HO(CH_2)_8OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 2.5 | -5 | |
| | | | | | 85.0 | 5.1 | -5 | 26.6 |
| .8 | $HO(CH_2)_9OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 2.5 | -5 | |
| | | | | | 85.0 | 6.2 | -5 | 26.6 |
| .9 | $HO(CH_2)_{10}OH + 2\ HBr$ | $C_6H_5OH$ | A = 0.05; B = 0.1; M = 0.5 | $k$AB | 75.9 | 2.3 | -5 | |

## LITERATURE

G.M. Bennett, F.M. Reynolds, *CSL* **1935**, 131.

# ESTER SOLVOLYSIS

## Alkyl ester of aliphatic carboxylic acid

*Liquid phase*

Reaction types:

$$\underset{(A)}{RCOOR'} + \underset{(B)}{R''OH} \rightarrow \underset{(L)}{RCOOH} + \underset{(M)}{R'OR''}$$

$$\underset{(A)}{RCOOR} + \underset{(B)}{OR''^{-}} \rightarrow \underset{(L)}{RCOO^{-}} + \underset{(M)}{R'OR''}$$

Amounts are in M/l.
Rates are in M/l per sec.
*Coded solvents, Comments, Literature, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Added (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCOOCH_3 + H_2O$ | MW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 25 | 1.0 | -3 | 15.6 | (0° - 140°) | | | (12) |
| .2 | $HCOOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 25 | 1.07 | -6 | 15.6 | (0° - 140°) | | | (12) |
| .3 | $HC(OC_2H_5)_3 + H_2O \rightarrow HCOOC_2H_5 + 2C_2H_5OH$ | | $H_2O + D_2O$ (N) | $c = H^+ + D^+$ | | $kAc$ | | | | | | | * | (2) |
| | | | 0.0 | | | | 15.0 | 3.83 | -6 | | | | | |
| | | | 0.925 | | | | " | 9.58 | -6 | | | | | |
| | | | 1.00 | | | | " | 1.03 | -5 | | | | | |
| | | | 0.0 | | | | 35.0 | 2.28 | -5 | 15.7 | | | | |
| | | | 0.917 | | | | " | 4.80 | -5 | | | | | |
| | | | 1.00 | | | | " | 5.28 | -5 | 14.3 | | | | |
| .4 | $CH_3COOCH_3 + H_2O$ | MW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 25 | 5.49 | -5 | 16.2 | (0° - 140°) | | | (12) |
| .5 | $CH_3COOCH_3 + H_2O$ | DW* | | HCl | 0.1 - 0.2 | $kA$ | | See Supplementary Table | | | | | | (8) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $CH_3COOCH_3 + H_2O$ | $H_2O$ | | HCl | 0.1 | $k\,A[HCl]$ | 25 | 1.06 | -4 | | | | | (8) |
| | | | | | " | | 35.3 | 3.23 | -4 | 17.1 | | | | " |
| | | | | | 0.2 | | 25 | 1.01 | -4 | | | | | " |
| | | " | ~ 0.7 | " | 0.1005 | $k\,A[HCl]$ | 25 | 1.09 | -4 | | | | * | (10) |
| | | | | | 0.5020 | | " | 1.17 | -4 | | | | | " |
| | | | | | 0.8275 | | " | 1.21 | -4 | | | | | " |
| | | | | | 1.800 | | " | 1.48 | -4 | | | | | " |
| | | | | | 2.429 | | " | 1.42 | -4 | | | | | " |
| | | | | | 0.1005 | | 35 | 2.77 | -4 | | | | | " |
| | | | | | 0.5020 | | " | 2.95 | -4 | | | | | " |
| | | | | | 0.8275 | | " | 3.07 | -4 | | | | | " |
| | | | | | 1.800 | | " | 3.50 | -4 | | | | | " |
| | | | | | 2.429 | | " | 3.73 | -4 | | | | | " |
| .7 | $CH_3COOCH_3 + H_2O$ | $H_2O$ | | $H_2SO_4$ | 0.7 | $k\,A$ | 15 | 3.17 | -5 | | | | | (9) |
| | | | | | | | 25 | 8.68 | -5 | 17.0 | | | | " |
| | | $D_2O$ 97 % | | " | 0.85 | " | 15 | 6.83 | -5 | | | | | " |
| | | | | | | | 25 | 1.67 | -4 | 15.8 | | | | " |
| .8 | $CH_3COOCH_3 + OH^-$ | MW* | A = B = 0.05 | | | $k\,AB$ | 25 | 1.37 | -1 | 11.5 | (0° - 140°) | | | (12) |
| .9 | $CH_3COOC_2H_5 + H_2O$ | $H_2O$ | | HCl | 0.1 | $k\,A[H^+]$ | 25 | 4.8 | -5 | | | | | (13) |
| | | | | | | | See Supplementary Table | | | | | | | |
| .10 | $CH_3COOC_2H_5 + H_2O$ | $H_2O$ | A = 0.4; L = 0.1 | | $k\,AL^{1/2} = k'AB[H^+]$ | | $k$ 25 | 4.34 | -7 | | | | * | (4) |
| | | | | | | | $k'$ 25 | 1.90 | -6 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $CH_3COOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 25 | 4.51 | -5 | | | | (17) | (3) |
| | | | | | | | 35 | 1.09 | -4 | | | | * | (3) |
| | | | | | | | 45 | 2.47 | -4 | 16.2 | 3.4 | 7 | | (3) |
| .12 | $CH_3COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | | – | $k\,AB$ | 20 | 4.54 | -3 | | | | | (16) |
| | | | | | | | 25 | 6.21 | -3 | | | | | (7) |
| | | | | | | | 30 | 1.09 | -2 | | | | | (16) |
| | | | | | | | 35 | 1.36 | -2 | | | | | (7) |
| | | | | | | | 40 | 2.30 | -2 | | | | | (16) |
| | | | | | | | 50 | 3.87 | -2 | 14.2 | | | | (7) |
| | | | | | | | " | 4.79 | -2 | 14.7 | | | | (16) |
| .13 | $CH_3COOC_2H_5 + OH^-$ | AW* | A = B = 0.1 | – | – | $k\,AB$ | 25 | 4.65 | -2 | | | | | (3) |
| | | | | | | | 35 | 8.22 | -2 | | | | | " |
| | | | | | | | 45 | 1.35 | -1 | | 7.9 | 5 | | " |
| .14 | $CH_3COOC_2H_5 + OC_2H_5^- + H_2O \rightarrow CH_3COO^- + 2C_2H_5OH$ | $H_2O$ + EtOH | 0.1 | – | – | $k\,A$ | 25 | See Supplementary Table | | | | | | (15) |
| .15 | $CH_3COOC(CH_3)_3 + OH^-$ | $H_2O$ | A = 0.014 – 0.019<br>B = 0.002 – 0.031 | | | $k\,AB$ | 6.6 | 4.1 | -4 | | | | | (22) |
| .16 | $CH_3COOCH_2C_6H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 15 | 1.15 | -5 | | | | | (21) |
| | | | | | | | 25 | 2.99 | -5 | | | | | " |
| | | | | | | | 40 | 1.23 | -4 | | | | | " |
| | | | | | | | 60 | 5.80 | -4 | | | | | " |
| | | | | | | | 80 | 2.28 | -3 | 16.4 | 3.8 | 7 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .17 | $CH_3COOCH_2C_6H_5 + OH^-$ | WA* | A = B = 0.05 | | | $kAB$ | -10 | 4.35 | -3 | | | | | ([21]) |
| | | | | | | | 0 | 1.02 | -2 | | | | | " |
| | | | | | | | 15 | 3.44 | -2 | | | | | " |
| | | | | | | | 25 | 6.99 | -2 | | | | | " |
| | | | | | | | 40 | 1.90 | -1 | 12.3 | 8.1 | 7 | | " |
| .18 | $CH_3COOCH_2(m\text{-}C_6H_4CH_3) + H_2O$ | WA* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 15 | 1.08 | -5 | | | | | ([21]) |
| | | | | | | | 25 | 2.83 | -5 | | | | | " |
| | | | | | | | 40 | 1.04 | -4 | | | | | " |
| | | | | | | | 60 | 4.69 | -4 | | | | | " |
| | | | | | | | 80 | 2.02 | -3 | 16.2 | 2.24 | 7 | | " |
| .19 | $CH_3COOCH_2(m\text{-}C_6H_4CH_3) + OH^-$ | WA* | A = B = 0.05 | - | - | $kAB$ | -10 | 3.31 | -3 | | | | | " |
| | | | | | | | 0 | 7.78 | -3 | | | | | " |
| | | | | | | | 15 | 2.63 | -2 | | | | | " |
| | | | | | | | 25 | 5.66 | -2 | | | | | " |
| | | | | | | | 40 | 1.50 | -1 | 12.4 | 7.6 | 7 | | " |
| .20 | $CH_3COOCH_2(p\text{-}C_6H_4CH_3) + H_2O$ | WA* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 25 | 2.98 | -5 | | | | | " |
| | | | | | | | 40 | 1.24 | -4 | | | | | " |
| | | | | | | | 60 | 5.71 | -4 | | | | | " |
| | | | | | | | 80 | 2.26 | -3 | 16.2 | 2.52 | 7 | | " |
| .21 | $CH_3COOCH_2(p\text{-}C_6H_4CH_3) + OH^-$ | WA* | A = B = 0.05 | - | - | $kAB$ | -10 | 2.95 | -3 | | | | | " |
| | | | | | | | 0 | 7.17 | -3 | | | | | " |
| | | | | | | | 15 | 2.36 | -2 | | | | | " |
| | | | | | | | 25 | 4.88 | -2 | | | | | " |
| | | | | | | | 40 | 1.37 | -1 | 12.5 | 7.6 | 7 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $k = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .22 | $CH_3COOCH_2(m\text{-}C_6H_4NO_2) + H_2O$ | WA* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 15 | 1.07 | -5 | | | | | (21) |
| | | | | | | | 25 | 2.55 | -5 | | | | | " |
| | | | | | | | 40 | 1.03 | -4 | | | | | " |
| | | | | | | | 60 | 4.94 | -4 | | | | | " |
| | | | | | | | 80 | 1.86 | -3 | 16.1 | 1.95 | 7 | | " |
| .23 | $CH_3COOCH_2(m\text{-}C_6H_4NO_2) + OH^-$ | WA* | A = B = 0.05 | - | - | $kAB$ | 15 | 1.98 | -1 | | | | | " |
| | | | | | | | 25 | 2.09 | -1 | | | | | " |
| | | | | | | | 40 | 5.65 | -1 | 11.6 | 6.13 | 7 | | " |
| .24 | $CH_3COOCH_2(p\text{-}C_6H_4NO_2) + H_2O$ | WA* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 15 | 1.07 | -5 | | | | | (21) |
| | | | | | | | 25 | 2.72 | -5 | | | | | " |
| | | | | | | | 40 | 1.07 | -4 | | | | | " |
| | | | | | | | 60 | 5.08 | -4 | | | | | " |
| | | | | | | | 80 | 1.98 | -3 | 16.2 | 2.46 | 7 | | " |
| .25 | $CH_3COOCH_2(p\text{-}C_6H_4NO_2) + OH^-$ | WA* | A = B = 0.05 | | | $kAB$ | 15 | 4.59 | -2 | | | | | (21) |
| | | | | | | | 25 | 1.37 | -1 | | | | | " |
| | | | | | | | 40 | 6.96 | -1 | 11.5 | 7.42 | 7 | | " |
| .26 | $CH_2ClCOOC_2H_5 + H_2O$ | EW* | | HCl | 0.05 | $kA[H^+]$ | 25 | 3.95 | -5 | | | | | (20) |
| | | | | | | | 40 | 1.35 | -4 | | | | | " |
| | | | | | | | 60 | 6.19 | -4 | | | | | " |
| | | | | | | | 80 | 2.26 | -3 | 15.3 | 7.25 | 6 | | " |
| .26.1 | $CH_2ClCOOCH(CH_3)_2 + OH^-$ | $H_2O$ | $10^4A = 4 - 8$<br>$10^4A = 4 - 7$ | | | $kAB$ | 6.6 | 2.0 | -1 | | | | | (22) |



942151 O—51——9

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .27 | $CHCl_2COOC_2H_5 + H_2O$ | EW* | | HCl | 0.05 | $kA[H^+]$ | 25 | 2.13 | -5 | | | | | ([20]) |
| | | | | | | | 40 | 6.59 | -5 | | | | | " |
| | | | | | | | 60 | 2.70 | -4 | | | | | " |
| | | | | | | | 80 | 9.25 | -4 | 14.3 | 6.6 | 5 | | " |
| .28 | $CCl_3COOC_2H_5 + H_2O$ | EW* | | HCl | 0.05 | $kA[H^+]$ | 25 | 8.26 | -5 | | | | | ([20]) |
| | | | | | | | 40 | 2.39 | -4 | | | | | " |
| | | | | | | | 60 | 7.61 | -4 | | | | | " |
| | | | | | | | 80 | 2.17 | -3 | 12.2 | 8.7 | 4 | | ([20]) |
| .29 | $N(CH_3)_2CH_2COOC(CH_3)_3 + OH^-$ | $H_2O$ | A = 0.008 - 0.016<br>B = 0.007 - 0.014 | | | $kAB$ | 10.2 | 3.72 | -4 | | | | | ([22]) |
| .30 | $Cl(CH_3)N(CH_3)_2CH_2COOC(CH_3)_3 + OH^-$ | $H_2O$ | A = 0.0004 - 0.002<br>B = 0.0004 - 0.002 | | | $kAB$ | 10.2 | 3.70 | -1 | | | | | ([22]) |
| .31 | $C_2H_5COOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 25 | 3.74 | -5 | | | | ([17]) | ([3]) |
| | | | | | | | 35.0 | 9.24 | -5 | | | | | ([3]) |
| | | | | | | | 44.7 | 2.07 | -4 | 16.2 | 2.9 | 7 | | " |
| .32 | $C_2H_5COOC_2H_5 + OH^-$ | AW* | A = B = 0.1 | | | $kAB$ | 24.8 | 2.20 | -2 | | | | | ([3]) |
| | | | | | | | 35.0 | 4.06 | -2 | | | | | |
| | | | | | | | 44.7 | 6.83 | -2 | | 1.2 | 6 | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .33 | $C_2H_5COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $kAB$ | 20 | 2.32 | -3 | | | | * | (16) |
| | | | | | | | 25 | 3.63 | -3 | | | | | (7) |
| | | | | | | | 30 | 5.30 | -3 | | | | | (16) |
| | | | | | | | 35 | 8.31 | -3 | | | | | (7) |
| | | | | | | | 40 | 1.17 | -2 | | | | | (16) |
| | | | | | | | 50 | 2.47 | -2 | 14.5 | | | | (7) |
| | | | | | | | " | 2.42 | -2 | 14.7 | | | | (16) |
| .34 | $C_2H_5COOC_2H_5 + OC_2H_5^- + H_2O \rightarrow C_2H_5COO^- + 2C_2H_5OH$ | Et85* | 0.05 | - | - | $kAB$ | 25 | 4.37 | -6 | | | | | (14) |
| .35 | $C_3H_7COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 1.14 | -5 | | | | * | (18) |
| | | | 0.05 - 0.1 | | 0.05 - 0.1 | | 25 | 1.83 | -5 | | | (17) (3) | | (18) |
| | | | 0.1 | | 0.1 | | 30 | 2.99 | -5 | | | | | (18) |
| | | | 0.05 | | 0.1 | | 35 | 4.83 | -5 | | | | | (3) |
| | | | 0.1 | | 0.1 | | 40 | 6.92 | -5 | 16.5 | | | | (18) |
| | | | 0.05 | | 0.05 | | 44.7 | 1.08 | -4 | 16.1 | 2.2 | 7 | | (3) |
| .36 | $C_3H_7COOC_2H_5 + OH^-$ | " | A = B = 0.1 | - | - | $kAB$ | 24.8 | 8.81 | -3 | | | | | (3) |
| | | | | | | | 35.0 | 1.68 | -2 | | | | | " |
| | | | | | | | 44.7 | 2.99 | -2 | | 1.3 | 7 | | " |
| .37 | $C_3H_7COOC_2H_5 + OH^-$ | Et85* | | - | - | $kAB$ | 20 | 1.18 | -3 | | | | | (16) |
| | | | | | | | 25 | 1.72 | -3 | | | | | (7) |
| | | | | | | | 30 | 2.79 | -3 | | | | | (16) |
| | | | | | | | 35 | 3.94 | -3 | | | | | (7) |
| | | | | | | | 40 | 6.27 | -3 | | | | | (16) |
| | | | | | | | 50 | 1.33 | -3 | 15.1 | | | | (7) |
| | | | | | | | " | 1.22 | -3 | 15.0 | | | | (16) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .38 | $(CH_3)_2CHCOOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 8.65 | -6 | | | | | (18) |
| | | | 0.05 - 0.1 | | 0.05 - 0.1 | | 25 | 1.40 | -5 | | | | (13) | (18) |
| | | | 0.1 | | 0.1 | | 30 | 2.07 | -5 | | | | | (18) |
| | | | 0.05 | | 0.05 | | 35 | 3.43 | -5 | | | | | (3) |
| | | | 0.1 | | 0.1 | | 40 | 5.03 | -5 | 16.4 | | | | (18) |
| | | | 0.05 | | 0.05 | | 44.7 | 7.46 | -5 | 15.3 | 2.5 | 6 | | (3) |
| .39 | $(CH_3)_2CHCOOC_2H_5 + OH^-$ | " | A = B = 0.1 | - | - | $kAB$ | 24.8 | 5.5 | -3 | | | | | (3) |
| | | | | | | | 35.0 | 1.03 | -2 | | | | | " |
| | | | | | | | 44.7 | 1.80 | -2 | | 1 | 6 | | " |
| .40 | $(CH_3)_2CHCOOC_2H_5 + OH^-$ | EW* | A = B = 0.05 | - | - | $kAB$ | 25 | 6.24 | -6 | 11.0 | | | | (3) |
| .41 | $(CH_3)_2CHCOOC_2H_5 + OH^-$ | Et85* | | - | - | $kAB$ | 25 | 8.01 | -4 | | | | | (7) |
| | | | | | | | 35 | 1.84 | -3 | | | | | " |
| | | | | | | | 50 | 5.72 | -3 | 14.5 | | | | " |
| .42 | $C_4H_9COOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 25 | 1.79 | -5 | | | | (17) | (3) |
| | | | | | | | 35 | 4.45 | -5 | | | | * | (3) |
| | | | | | | | 45 | 1.02 | -4 | 16.5 | 2.2 | 7 | | " |
| .43 | $C_4H_9COOC_2H_5 + OH^-$ | " | A = B = 0.1 | - | - | $kAB$ | 24.8 | 6.59 | -3 | | | | | (3) |
| | | | | | | | 35.0 | 1.33 | -2 | | | | | " |
| | | | | | | | 44.7 | 2.45 | -2 | | 7.9 | 6 | | " |
| .44 | $C_4H_9COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $kAB$ | 25 | 1.92 | -3 | | | | | (7) |
| | | | | | | | 35 | 4.42 | -3 | | | | | " |
| | | | | | | | 50 | 1.33 | -2 | 14.7 | | | | " |
| .45 | $(CH_3)_2CHCH_2COOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 24.8 | 5.72 | -6 | | | | | (3) |
| | | | | | | | 35.0 | 1.46 | -5 | | | | | " |
| | | | | | | | 44.7 | 3.30 | -5 | 16.5 | 7.4 | 6 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .46 | $(CH_3)_2CHCH_2COOC_2H_5 + OH^-$ | AW* | A = B = 0.1 | | – | $k$AB | 24.8 | 2.18 | -3 | | | | | (3) |
| | | | | | | | 35.0 | 4.50 | -3 | | | | | " |
| | | | | | | | 44.7 | 8.63 | -3 | | 1.3 | 7 | | " |
| .47 | $(CH_3)_2CHCH_2COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | – | – | $k$AB | 25 | 4.27 | -4 | | | | | (7) |
| | | | | | | | 35 | 1.02 | -3 | | | | | " |
| | | | | | | | 50 | 3.34 | -3 | 15.7 | | | | " |
| .48 | $C_2H_5CH(CH_3)COOC_2H_5 + OH^-$ | " | " | – | – | $k$AB | 25 | 3.08 | -4 | | | | | (7) |
| | | | | | | | 35 | 7.35 | -4 | | | | | " |
| | | | | | | | 50 | 2.36 | -3 | 15.4 | | | | " |
| .49 | $(CH_3)_3CCOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $k$A[$H^+$] | 24.8 | 1.28 | -6 | | | | | (3) |
| | | | | | | | 35.0 | 3.63 | -6 | | | | | " |
| | | | | | | | 44.7 | 1.10 | -5 | | | | | " |
| .50 | $(CH_3)_3CCOOC_2H_5 + OH^-$ | " | A = B = 0.1 | – | – | $k$AB | 24.8 | 2.23 | -4 | | | | | (3) |
| | | | | | | | 35.0 | 4.56 | -4 | | | | | " |
| | | | | | | | 44.7 | 8.74 | -4 | | 7.9 | 5 | | " |
| .51 | $(CH_3)_3CCOOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | – | – | $k$AB | 25 | 2.54 | -5 | | | | | (7) |
| | | | | | | | 35 | 6.35 | -5 | | | | | " |
| | | | | | | | 50 | 2.41 | -4 | 16.5 | | | | " |
| .52 | $C_5H_{12}COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $k$A[$H^+$] | 20 | 1.10 | -5 | | | | | (18) |
| | | | 0.05 – 0.1 | | 0.05 – 0.1 | | 25 | 1.77 | -5 | | | | (3) | (18) |
| | | | 0.1 | | 0.1 | | 30 | 2.81 | -5 | | | | | (18) |
| | | | 0.05 | | 0.05 | | 35 | 4.30 | -5 | | | | | (3) |
| | | | 0.1 | | 0.1 | | 40 | 6.72 | -5 | 16.4 | | | | (18) |
| | | | 0.05 | | 0.05 | | 44.7 | 9.76 | -5 | 16.2 | 1.35 | 7 | | (3) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .53 | $C_5H_{11}COOC_2H_5 + OH^-$ | Et85* | | - | - | $kAB$ | 25 | 2.07 | -3 | | | | | (7) |
| | | | | | | | 35 | 4.81 | -3 | | | | | " |
| | | | | | | | 50 | 1.45 | -2 | 14.8 | | | | " |
| .54 | $(CH_3)_2CHCH_2CH_2COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $kAB$ | 25 | 4.11 | -4 | | | | | (16) |
| | | | | | | | 35 | 9.63 | -4 | | | | | " |
| | | | | | | | 45 | 2.20 | -4 | | | | | " |
| | | | | | | | 55 | 4.65 | -3 | 15.7 | | | | " |
| .54.1 | $(CH_3)_2CHCH_2CH_2COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 1.04 | -5 | | | | | (18) |
| | | | | | | | 25 | 1.68 | -5 | | | | | |
| | | | | | | | 30 | 2.68 | -5 | | | | | |
| | | | | | | | 40 | 6.16 | -5 | | | | | |
| | | | | | | | 50 | 1.45 | -4 | 16.4 | | | | |
| .55 | $C_2H_5CH(CH_3)CH_2COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $kAB$ | 25 | 1.86 | -3 | | | | | (16) |
| | | | | | | | 35 | 4.31 | -3 | | | | | " |
| | | | | | | | 45 | 9.04 | -3 | | | | | " |
| | | | | | | | 55 | 1.89 | -2 | 15.0 | | | | " |
| .56 | $(C_2H_5)_2CHCOOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 24.8 | 1.17 | -6 | | | | | (3) |
| | | | | | | | 35.0 | 3.33 | -6 | | | | | " |
| | | | | | | | 44.7 | 8.69 | -6 | 19.1 | 1.2 | 8 | | " |
| .57 | $(C_2H_5)_2CHCOOC_2H_5 + OH^-$ | AW* | A = B = 0.1 | - | - | $kAB$ | 24.8 | 8.3 | -5 | | | | | (3) |
| | | | | | | | 35.0 | 1.84 | -4 | | | | | " |
| | | | | | | | 44.7 | 3.71 | -4 | | 2.5 | 6 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .58 | $(C_2H_5)_2CHCOOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | – | – | $kAB$ | 25 | 1.53 | -5 | | | | (16) | (7) |
| | | | | | | | 35 | 4.35 | -5 | | | | " | " |
| | | | | | | | 45 | 9.70 | -5 | | | | * | (16) |
| | | | | | | | 50 | 1.54 | -4 | | | | | (7) |
| | | | | | | | 55 | 2.15 | -4 | 17.3 | | | | (16) |
| .58.1 | $CH_3COC(CH_3)_2COOC_2H_5 + OH^-$ | $H_2O$ | A = 0.03 | | | $kAB$ | 0.0 | 8.1 | -4 | | | | | (12a) |
| | | | B = 0.03 – 0.04 | | | | 24.9 | 4.2 | -3 | | | | | |
| .59 | $C_6H_{13}COOC_2H_5 + H_2O$ | AW* | 0.05 | HCl | 0.05 | $kA[H^+]$ | 24.8 | 1.64 | -5 | | | | | (3) |
| | | | | | | | 35.0 | 4.09 | -5 | | | | | " |
| | | | | | | | 44.7 | 9.07 | -5 | 16.2 | 1.3 | 7 | | " |
| .60 | $C_6H_{13}COOC_2H_5 + OH^-$ | " | A = B = 0.05 | – | – | $kAB$ | 24.8 | 6.08 | -3 | | | | | (3) |
| | | | | | | | 35.0 | 1.19 | -2 | | | | | " |
| | | | | | | | 44.7 | 2.21 | -2 | | 7.9 | 6 | | " |
| .61 | $C_6H_{13}COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | – | – | $kAB$ | 25 | 1.79 | -3 | | | | | (7) |
| | | | | | | | 35 | 4.06 | -3 | | | | | " |
| | | | | | | | 50 | 1.27 | -2 | | | | | " |
| .61.1 | $C_3H_7CH(CH_3)CH_2COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 2.50 | -6 | | | | | (18) |
| | | | | | | | 25 | 4.05 | -6 | | | | | |
| | | | | | | | 30 | 6.46 | -6 | | | | | |
| | | | | | | | 40 | 1.52 | -5 | | | | | |
| | | | | | | | 50 | 3.55 | -5 | 16.4 | | | | |
| .62 | $C_7H_{15}COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 24.8 | 1.55 | -5 | | | | | (3) |
| | | | | | | | 35.0 | 3.85 | -5 | | | | | " |
| | | | | | | | 44.7 | 8.70 | -5 | 16.3 | 1.4 | 7 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .63 | $C_7H_{15}COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $k$AB | 25 | 1.84 | -3 | | | | | (7) |
| | | | | | | | 35 | 4.30 | -3 | | | | | " |
| | | | | | | | 45 | 1.33 | -2 | 15.0 | | | | " |
| .64 | $(C_3H_7)_2CHCOOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $k$AB | 25 | 1.0 | -5 | | | | | (17) |
| | | | | | | | 35 | 2.8 | -5 | | | | | " |
| | | | | | | | 45 | 6.5 | -5 | | | | | " |
| | | | | | | | 55 | 1.54 | -4 | 17.2 | | | | " |
| .64.1 | $C_8H_{17}COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $k$A[$H^+$] | 20 | 8.68 | -6 | | | | | (18) |
| | | | | | | | 25 | 1.40 | -5 | | | | | |
| | | | | | | | 30 | 2.20 | -5 | | | | | |
| | | | | | | | 40 | 5.19 | -5 | | | | | |
| | | | | | | | 50 | 1.18 | -4 | 16.4 | | | | |
| .65 | $(C_4H_9)_2CHCOOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $k$A | 25 | 1.0 | -5 | | | | | (17) |
| | | | | | | | 35 | 2.5 | -5 | | | | | " |
| | | | | | | | 45 | 6.3 | -5 | | | | | " |
| | | | | | | | 55 | 1.53 | -4 | 17.7 | | | | " |
| .66 | $C_{11}H_{23}COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | - | - | $k$AB | 25 | 1.84 | -3 | | | | | (17) |
| | | | | | | | 35 | 4.11 | -3 | | | | | " |
| | | | | | | | 45 | 9.27 | -3 | | | | | " |
| | | | | | | | 55 | 1.87 | -2 | 15.1 | | | | " |
| **Cycloalkyl-substituted aliphatic carboxylic acid** | | | | | | | | | | | | | | |
| .67 | *cyclo*-$C_6H_{11}CH_2COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $k$A[$H^+$] | 20 | 3.00 | -6 | | | | | (17) |
| | | | | | | | 25 | 4.81 | -6 | | | | | " |
| | | | | | | | 30 | 7.80 | -6 | | | | | " |
| | | | | | | | 40 | 1.90 | -5 | | | | | " |
| | | | | | | | 50 | 4.41 | -5 | 16.9 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .68 | *cyclo*-$C_6H_{11}CH_2COOC_2H_5 + OH^-$ | Et85* | 0.05 | – | – | $kAB$ | 25 | 5.09 | -4 | | | | | (17) |
| | | | | | | | 65 | 1.16 | -2 | 15.6 | | | | " |
| | **Aryl-substituted aliphatic carboxylic acid** | | | | | | | | | | | | | |
| .69 | $C_6H_5CH_2COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 9.34 | -6 | | | | * | (17) |
| | | | | | | | 25 | 1.52 | -5 | | | | | (17)(3) |
| | | | | | | | 30 | 2.37 | -5 | | | | | (17) |
| | | | | | | | 35.0 | 3.84 | -5 | | | | | (3) |
| | | | | | | | 40 | 5.50 | -5 | | | | | (17) |
| | | | | | | | 44.7 | 8.84 | -5 | 16.2 | 1.2 | 7 | | (3) |
| | | | | | | | 50 | 1.20 | -4 | 16.1 | | | | (17) |
| .70 | $C_6H_5CH_2COOC_2H_5 + OH^-$ | Et85* | 0.05 | – | – | $kAB$ | 25 | 1.01 | -2 | | | | | (17) |
| | | | | | | | 55 | 8.83 | -2 | 14.1 | | | | " |
| .71 | $(C_6H_5)_2CHCOOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 2.96 | -8 | | | | | (17) |
| | | | | | | | 25 | 5.03 | -8 | | | | | " |
| | | | | | | | 30 | 8.36 | -8 | | | | | " |
| | | | | | | | 40 | 2.09 | -7 | | | | | " |
| | | | | | | | 50 | 5.06 | -7 | 17.7 | | | | " |
| .72 | $(C_6H_5)_2CHCOOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | | – | $kAB$ | 25 | 5.60 | -4 | | | | | (17) |
| | | | | | | | 65 | 1.37 | -2 | 16.0 | | | | " |
| .73 | $CH_3CH(C_6H_5)COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 1.71 | -7 | | | | | (17) |
| | | | | | | | 25 | 2.77 | -7 | | | | | " |
| | | | | | | | 30 | 4.47 | -7 | | | | | " |
| | | | | | | | 40 | 1.11 | -6 | | | | | " |
| | | | | | | | 50 | 2.51 | -6 | 16.9 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .74 | $CH_3CH(C_6H_5)COOC_2H_5 + H_2O$ | Et85* | 0.05 | - | - | $kAB$ | 25 | 8.02 | -4 | | | | | ([17]) |
| | | | | | | | 65 | 1.76 | -2 | 15.4 | | | | " |
| .75 | $C_2H_5CH(C_6H_5)COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 6.69 | -8 | | | | | ([17]) |
| | | | | | | | 25 | 1.10 | -7 | | | | | " |
| | | | | | | | 30 | 1.78 | -7 | | | | | " |
| | | | | | | | 40 | 4.33 | -7 | | | | | " |
| | | | | | | | 50 | 1.03 | -6 | 17.1 | | | | " |
| .76 | $C_2H_5CH(C_6H_5)COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | | - | $kAB$ | 25 | 2.64 | -4 | | | | | ([17]) |
| | | | | | | | 65 | 6.28 | -3 | 15.9 | | | | " |
| .77 | $C_6H_5(CH_2)_2COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 8.05 | -6 | | | | | ([17]) |
| | | | | | | | 25 | 1.28 | -5 | | | | | " |
| | | | | | | | 30 | 2.05 | -5 | | | | | " |
| | | | | | | | 40 | 4.76 | -5 | | | | | " |
| | | | | | | | 50 | 1.10 | -4 | 16.3 | | | | " |
| .78 | $C_6H_5(CH_2)_2COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | | - | $kAB$ | 25 | 5.04 | -3 | | | | | ([17]) |
| | | | | | | | 55 | 4.71 | -2 | 14.5 | | | | " |
| .79 | $C_6H_5(CH_2)_3COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 8.00 | -6 | | | | | ([17]) |
| | | | | | | | 25 | 1.27 | -5 | | | | | " |
| | | | | | | | 30 | 2.04 | -5 | | | | | " |
| | | | | | | | 40 | 4.86 | -5 | | | | | " |
| | | | | | | | 50 | 1.12 | -4 | 16.5 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .80 | $C_6H_5(CH_2)_3COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | | | $kAB$ | 25 | 2.69 | -3 | | | | | (17) |
| | | | | | | | 55 | 2.68 | -2 | 14.7 | | | | " |
| .81 | $C_6H_5(CH_2)_4COOC_2H_5 + H_2O$ | AW* | 0.1 | HCl | 0.1 | $kA[H^+]$ | 20 | 8.61 | -6 | | | | | (17) |
| | | | | | | | 25 | 1.39 | -5 | | | | | " |
| | | | | | | | 30 | 2.24 | -5 | | | | | " |
| | | | | | | | 40 | 5.35 | -5 | | | | | " |
| | | | | | | | 50 | 1.21 | -4 | 16.6 | | | | " |
| .82 | $C_6H_5(CH_2)_4COOC_2H_5 + OH^-$ | Et85* | A = B = 0.05 | | | $kAB$ | 25 | 2.28 | -3 | | | | | (17) |
| | | | | | | | 55 | 2.19 | -2 | 14.7 | | | | " |

## SUPPLEMENTARY TABLES

(.5) $CH_3COOCH_3 + H_2O$ ([8])

Solvent DW* = 1, 4 - dioxane + $H_2O$ ($x$ %)

| HCl | °C | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $x$ = | 0 | 10 | 20 | 30 | 45 | | 75 | 80 | 90 |
| 0.1 | 25 | $10^4 k$ = | 1.06 | 1.15 | 1.51 | 1.12 | 1.00 | | 0.728 | 0.622 | 0.764 |
| | | $E$ = | 17.1 | 16.5 | 16.1 | 16.0 | - | | - | 15.4 | 16.5 |
| 0.1 | 35.3 | $x$ = | 0 | 9 | 20 | 40 | 60 | | | 80 | 90 |
| | | $10^4 k$ = | 3.23 | 2.92 | 2.99 | 2.83 | 2.20 | | | 1.88 | 2.10 |
| 0.2 | 25 | $x$ = | 0 | 10 | 20 | | 60 | 70 | | 80 | 90 |
| | | $10^4 k$ = | 1.01 | 1.10 | 1.16 | | 0.884 | 0.744 | | 0.669 | 0.758 |

(.9) $CH_3COOC_2H_5 + H_2O$ ([13])

Salt effects (selected data); HCl = 0.1

| Salt | M/l | $10^6 k$ | Salt | M/l | $10^6 k$ | Salt | M/l | $10^6 k$ |
|---|---|---|---|---|---|---|---|---|
| NaCl | 1 | 5.82 | LiBr | 1 | 4.80 | $BaCl_2$ | 0.33 | 4.96 |
| | 4 | 9.78 | | 3 | 3.65 | | 1.33 | 6.37 |
| $NaNO_3$ | 1 | 5.10 | NaBr | 2 | 5.93 | $Ca(NO_3)_2$ | 1.06 | 5.15 |
| | 6 | 5.83 | | 5 | 7.56 | | 2.25 | 5.50 |

## SUPPLEMENTARY TABLES *(continued)*

(.14) $CH_3COOC_2H_5 + OC_2H_5^- + H_2O \rightarrow CH_3COO^- + 2C_2H_5OH$ ([15])

Solvent: $H_2O + C_2H_5OH$ ($x$ %)

| $x$ | 0 | 20 | 40 | 50 | 65 | 75 | 96 |
|---|---|---|---|---|---|---|---|
| $10^6 k$ | 100 | 81.8 | 48.4 | 35.0 | 20.0 | 12.0 | 1.83 |

## SOLVENTS

MW* $CH_3OH + H_2O$ 40 ml/100 ml solution ([12])

EW* $C_2H_5OH + H_2O$ 40 ml/100 ml solution ([12])

DW* 1, 4-dioxane + $H_2O$ ($x$ %)

Et85* $C_2H_5OH$ 85 % + $H_2O$ 15 % ([7])([14])([16])([17])

AW* $(CH_3)_2CO$ 70 % + $H_2O$ 30 % ( = ~ 56 wt % $(CH_3)_2CO$) ([3])([17])

WA* $(CH_3)_2CO + H_2O$ 40 ml/100 ml solution ([21])

## COMMENTS

**General.** Activation entropy calculations, see ([17]).

**(.3)** Original time unit presumed to be min, on the basis of other papers of the same author; converted to sec. Value of $k$ for 100 % $D_2O$ is extrapolated. The rate is also represented in a two-term formula, $(k_H[H^+] + k_D[D^+])A$; for the calculation of $[H^+]$ and $[D^+]$ separately, see ([2]) p. 613. **(.7)** Viscosity measurements. **(.10)** $k$ constant over half of the reaction, then falls slowly. The rate equation accounts for the increasing catalysis by the $H^+$ ions of L,, with $[H^+] = (KL)^{1/2}$, where $K = 1.85 \times 10^{-5}$. **(.11)** $k$ at 25°C average of close data of ([17]) and ([3]). **(.12)** Combined data of ([16]) and ([7]) at temperatures alternating by 5°C; agreement satisfactory. **(.14)** Electric conductivity measurements. **(.31) (.35) (.42) (.69)** as (.11); Data of ([3]) and of ([18]) at temperatures alternating by 5°C, in good agreement. **(.37)** as (.12). **(.38) (.52)** Data of ([3]) and ([16]) at temperatures alternating by 5°C, in good agreement. **(.58)** $k$ at 25 and 35°C average of close data of ([16]) and ([7]).

## LITERATURE

([1]) F.Brescia, V.K.LaMer, *ACS* 1930, **60**, 1962. ([2]) F.Brescia, V.K.LaMer, 1940, **62**, 612. ([3]) G.Davies, D.P.Evans, *CSL* **1940**, 339. ([4]) H.M.Dawson, W.Lowson, *CSL* **1927**, 2107. ([5]) A.de Hemptinne, *ZPC* 1899, **31**, 35. ([6]) A.de Hemptinne, *ZPC* 1900, **34**, 676. ([7]) D.P.Evans, J.J.Gordon, H.W.Watson, *CSL* **1938**, 1439. ([8]) H.S.Harned, A.M.Ross, *ACS* 1941, **63**, 1993. ([9]) J.C.Hornel, J.A.V.Butler, *CSL* **1936**, 1361. ([10]) A.Lamble, W.C.MacLewis, *CSL* 1914, **105**, 2330. ([11]) H.Ley, *ZPC* 1899, **30**, 193. ([12]) W.B.S.Newling, C.N.Hinshelwood, *CSL* **1936**, 1357. ([12a]) K.J.Pedersen, *ACS* 1938, **58**, 240. ([13]) R.A.Robinson, *TFS* 1930, **26**, 217. ([14]) R.F.W.Selman, *TFS* 1930, **26**, 7. ([15]) R.F.W.Selman, F.Bainbridge Fletcher, *TFS* 1929, **25**, 423. ([16]) H.A.Smith, H.S.Levenson, *ACS* 1939, **61**, 1172. ([17]) H.A.Smith, R.R.Myers, *ACS* 1942, **64**, 2362; H.S.Levenson, H.A.Smith, *ACS* 1940, **62**, 1556; H.S.Levenson, H.A.Smith, *ACS* 1940, **62**, 2324. ([18]) H.A.Smith, J.S.Steele, *ACS* 1941, **63**, 3466. ([19]) H.S.Taylor, *ACS* 1915, **37**, 551. ([20]) E.W.Timm, C.N.Hinshelwood, *CSL* **1938**, 862.

([21]) E.Tommila, C.N.Hinshelwood, *CSL* **1938**, 1801. ([22]) F.H.Westheimer, M.W.Shookhoff, *ACS* 1940, **52**, 269.

# ESTER SOLVOLYSIS

## Aromatic carboxylic acid and Aliphatic alcohol

*Liquid phase*

Reaction types

$$\underset{(A)}{ArCOOR} + \underset{(B)}{R'OH} \quad \underset{(L)}{ArCOOH} + \underset{(M)}{ROR'}$$

$$\underset{(A)}{ArCOOR} + \underset{(B)}{OR'^{-}} \quad \underset{(L)}{ArCOO^{-}} + \underset{(M)}{ROR'}$$

Amounts are in M/l.
Rates in M/l per sec.

*Coded solvents, Comments, Literature, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5COOCH_3 + H_2O$ | MW* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 25 | 2.67 | -5 | | | | | (5) |
| | | | | | | | 100 | 1.68 | -4 | | | | | (7) |
| | | | | | | | 121 | 5.56 | -4 | | | | | " |
| | | | | | | | 139 | 1.56 | -3 | | | | | " |
| | | | | | | | 154 | 3.21 | -3 | 17.6 | 3.7 | 6 | | (7) |
| .2 | $C_6H_5COOCH_3 + OH^-$ | WA* | A = B = 0.05 | | - | $k AB$ | 0 | 1.00 | -3 | | | | | (8) |
| | | | | | | | 15 | 4.04 | -3 | | | | | " |
| | | | | | | | 25 | 9.01 | -3 | | | | | " |
| | | | | | | | 40 | 2.89 | -2 | 14.2 | 2.4 | 8 | | (8) |
| .3 | $C_6H_5COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 25 | 1.29 | -7 | | | | | (5) |
| | | | | | | | 60 | 3.92 | -6 | | | | | (7) |
| | | | | | | | 80 | 2.05 | -5 | | | | | " |
| | | | | | | | 100 | 8.45 | -5 | | | | | " |
| | | | | | | | 120 | 3.35 | -4 | | | | | " |
| | | | | | | | 138 | 1.14 | -3 | 19.6 | 2.8 | 7 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $C_6H_5COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 80 | 2.09 | -5 | | | | | (7) |
| | | | | | | | 100 | 9.44 | -5 | | | | | " |
| | | | | | | | 121 | 3.95 | -4 | | | | | " |
| | | | | | | | 139 | 1.28 | -3 | 20.2 | 6.9 | 7 | | " |
| .5 | $C_6H_5COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | | $k\,AB$ | 0 | 3.02 | -4 | | | | | (8) |
| | | | | | | | 15 | 1.27 | -3 | | | | | " |
| | | | | | | | 25 | 2.87 | -3 | | | | | " |
| | | | | | | | 40 | 9.56 | -3 | 14.6 | 1.5 | 8 | | " |
| .6 | $C_6H_5COOC_2H_5 + OH^-$ | S* | A = B = 0.05 | | | $k\,AB$ | see Supplementary Table | | | | | | | (2) |
| .7 | $C_6H_5COOC_2H_5 + OH^-$ | Et85* | | | | $k\,AB$ | 25 | 5.85 | -4 | | | | (3) | (1) |
| | | | | | | | 35 | 1.68 | -3 | | | | * | (1) |
| | | | | | | | 50 | 6.28 | -3 | 17.7 | | | | " |
| | | | | | | | 50 | 5.60 | -3 | | | | | (3) |
| .8 | $C_6H_5C^{14}OOC_2H_5 + OH^-$ | Et50* | A = 0.09<br>B = 0.5 | | | $k\,AB$ | | $k^{14}/k$ | | | | | | |
| | | | | | | | 25 | 0.86 | | | | | | (6) |
| .9 | $o\text{-}CH_3C_6H_4COOC_2H_5 + OH^-$ | Et85* | | | | $k\,AB$ | 25 | 7.76 | -5 | | | | | (1) |
| | | | | | | | 35 | 2.07 | -4 | | | | | " |
| | | | | | | | 50 | 8.09 | -4 | 18.0 | | | | " |
| .10 | $m\text{-}CH_3C_6H_4COOC_2H_5 + OH^-$ | Et85* | | | | $k\,AB$ | 25 | 4.33 | -4 | | | | | (1) |
| | | | | | | | 35 | 1.18 | -3 | | | | | " |
| | | | | | | | 50 | 4.57 | -3 | 17.9 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $m$-$CH_3C_6H_4COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | | $k$AB | 0 | 1.64 | -4 | | | | | ([8]) |
| | | | | | | | 15 | 7.22 | -4 | | | | | " |
| | | | | | | | 25 | 1.71 | -3 | | | | | " |
| | | | | | | | 40 | 5.56 | -3 | 14.9 | 1.5 | 8 | | " |
| .12 | $p$-$CH_3C_6H_4COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k$A[$H^+$] | 80 | 1.68 | -5 | | | | | ([7]) |
| | | | | | | | 100 | 8.31 | -5 | | | | | " |
| | | | | | | | 120 | 3.49 | -4 | | | | | " |
| | | | | | | | 139 | 1.05 | -3 | 20.4 | 7.5 | 7 | | " |
| .13 | $p$-$CH_3C_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k$A[$H^+$] | 60 | 3.24 | -6 | | | | | ([7]) |
| | | | | | | | 80 | 1.65 | -5 | | | | | " |
| | | | | | | | 100 | 8.19 | -5 | | | | | " |
| | | | | | | | 120 | 3.01 | -4 | | | | | " |
| | | | | | | | 140 | 9.78 | -4 | 19.7 | 2.9 | 7 | | " |
| .14 | $p$-$CH_3C_6H_4COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | - | $k$AB | 0 | 1.06 | -4 | | | | | ([8]) |
| | | | | | | | 15 | 4.77 | -4 | | | | | " |
| | | | | | | | 25 | 1.16 | -3 | | | | | " |
| | | | | | | | 40 | 3.90 | -3 | 15.2 | 1.6 | 8 | | " |
| .15 | $p$-$CH_3C_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | - | $k$A | 25 | 2.51 | -4 | | | | | ([3]) |
| | | | B = 0.005 | | | | 50 | 2.71 | -3 | 18.2 | 5.7 | 9 | | " |



942151 O—51——10

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .16 | $p$-$CH_3OC_6H_4COOCH_3 + H_2O$ | MW* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 100 | 1.09 | -4 | | | | | (7) |
| | | | | | | | 120 | 3.92 | -4 | | | | | " |
| | | | | | | | 138 | 1.01 | -3 | | | | | " |
| | | | | | | | 154 | 2.59 | -3 | 18.3 | 5.3 | 6 | | " |
| .17 | $p$-$CH_3OC_6H_4COOCH_3 + OH^-$ | WA* | A = B = 0.05 | | | $k\,AB$ | 0 | 2.00 | -4 | | | | | (8) |
| | | | | | | | 15 | 9.04 | -4 | | | | | " |
| | | | | | | | 25 | 2.22 | -3 | | | | | " |
| | | | | | | | 40 | 7.70 | -3 | 15.4 | 5.1 | 8 | | " |
| .18 | $p$-$CH_3OC_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 60 | 2.05 | -6 | | | | | (7) |
| | | | | | | | 80 | 1.41 | -5 | | | | | " |
| | | | | | | | 99 | 5.65 | -5 | | | | | " |
| | | | | | | | 120 | 2.57 | -4 | | | | | " |
| | | | | | | | 138 | 8.00 | -4 | 20.5 | 6.9 | 7 | | " |
| .19 | $p$-$CH_3OC_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1<br>B = 0.005 | | | $k\,AB$ | 25 | 1.15 | -4 | | | | | (3) |
| | | | | | | | 50 | 1.31 | -3 | 18.6 | 5.4 | 9 | | " |
| .20 | $p$-$CH_3OC_6H_4COOC_2H_5 + OH^-$ | EW* | A = B = 0.05 | | | $k\,AB$ | 25 | 7.9 | -4 | 15.3<br>(0°-40°) | | | | (5) |
| .21 | $2$-$CH_3$-$5$-$(CH_3)_2CH\,C_6H_3 + OH^-$ | Et85* | | | | $k\,AB$ | 25 | 5.75 | -5 | | | | | (4) |
| | | | | | | | 35 | 1.47 | -4 | | | | | " |
| | | | | | | | 50 | 7.00 | -4 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .22 | $2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CH.C_6H_3COOC_2H_5 + OH^-$ | Et85* | | - | - | $k\,AB$ | 25 | 5.75 | -5 | | | | | ([4]) |
| | | | | | | | 35 | 1.32 | -4 | | | | | " |
| | | | | | | | 50 | 5.35 | -4 | | | | | " |
| .23 | $3\text{-}CH_3\text{-}6\text{-}(CH_3)_2CH.C_6H_3COOCH_3 + OH^-$ | Et85* | | - | - | $k\,AB$ | 25 | 2.35 | -5 | | | | | ([4]) |
| | | | | | | | 35 | 6.59 | -5 | | | | | " |
| | | | | | | | 50 | 3.73 | -4 | | | | | " |
| .24 | $3\text{-}CH_3\text{-}6\text{-}(CH_3)_2CH.C_6H_3COOC_2H_5 + OH^-$ | Et85* | | - | - | $k\,AB$ | 25 | 2.18 | -5 | | | | | ([4]) |
| | | | | | | | 35 | 6.45 | -2 | | | | | " |
| | | | | | | | 50 | 2.45 | -4 | | | | | " |
| .25 | $p\text{-}OHC_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 80 | 9.92 | -6 | | | | | ([7]) |
| | | | | | | | 100 | 4.16 | -5 | | | | | " |
| | | | | | | | 120 | 1.91 | -4 | 20.4 | 4.1 | 7 | | ([7]) |
| | | | | | | | 138 | 6.70 | -4 | | | | | " |
| .26 | $p\text{-}OHC_6H_4COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 80 | 9.82 | -6 | | | | | ([7]) |
| | | | | | | | 100 | 4.69 | -5 | | | | | " |
| | | | | | | | 120 | 1.96 | -4 | | | | | " |
| | | | | | | | 139 | 6.68 | -4 | 20.7 | 6.7 | 7 | | " |
| .27 | $m\text{-}NH_2C_6H_4COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | | $k\,AB$ | 0 | 1.59 | -4 | | | | | ([8]) |
| | | | | | | | 15 | 7.26 | -4 | | | | | " |
| | | | | | | | 25 | 1.65 | -3 | | | | | " |
| | | | | | | | 40 | 5.60 | -3 | 15.0 | 1.8 | 8 | | " |

212.442.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .28 | $p$-$NH_2C_6H_4COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | | $k$AB | 25 | 8.40 | -5 | | | | | ([8]) |
| | | | | | | | 40 | 2.41 | -4 | | | | | " |
| | | | | | | | 60 | 1.74 | -3 | | | | | " |
| | | | | | | | 80 | 7.14 | -2 | 16.7 | 1.7 | 8 | | " |
| .29 | $p$-$NH_2C_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1<br>B = 0.005 | | | $k$AB | 25 | 1.27 | -5 | | | | | ([3]) |
| | | | | | | | 50 | 1.72 | -4 | 20.0 | 5.42 | 9 | | " |
| .30 | $o$-$NO_2C_6H_4COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k$A[$H^+$] | 80 | 1.46 | -6 | | | | | ([7]) |
| | | | | | | | 100 | 7.04 | -6 | | | | | " |
| | | | | | | | 121 | 3.72 | -5 | | | | | " |
| | | | | | | | 139 | 1.08 | -4 | 21.1 | 1.6 | 7 | | " |
| .31 | $o$-$NO_2C_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k$A[$H^+$] | 80 | 1.49 | -6 | | | | | ([7]) |
| | | | | | | | 100 | 5.91 | -6 | | | | | " |
| | | | | | | | 121 | 2.62 | -5 | | | | | " |
| | | | | | | | 139 | 8.56 | -5 | 20.1 | | | | " |
| .32 | $o$-$NO_2C_6H_4COOC_2H_5 + OH^-$ | Et85* | | - | - | $k$AB | 25 | 5.41 | -3 | | | | | ([1]) |
| | | | | | | | 35 | 1.27 | -2 | | | | | " |
| | | | | | | | 50 | 3.88 | -2 | 14.5 | | | | " |
| .33 | $m$-$NO_2C_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k$A[$H^+$] | 25 | 1.10 | -7 | | | | | ([5]) |
| | | | | | | | 80 | 2.09 | -7 | | | | | ([7]) |
| | | | | | | | 100 | 8.85 | -5 | | | | | " |
| | | | | | | | 120 | 3.32 | -4 | | | | | " |
| | | | | | | | 138 | 9.00 | -4 | 18.8 | 9.5 | 6 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .34 | $m\text{-}NO_2C_6H_4COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.06 | $k\,A[H^+]$ | 60 | 3.48 | -6 | | | | | (7) |
| | | | | | | | 80 | 1.93 | -5 | | | | | " |
| | | | | | | | 100 | 8.64 | -5 | | | | | " |
| | | | | | | | 120 | 3.68 | -4 | | | | | " |
| | | | | | | | 139 | 1.15 | -3 | 20.1 | 5.3 | 7 | | " |
| .35 | $m\text{-}NO_2C_6H_4COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | | $k\,AB$ | 0 | 1.65 | -4 | | | | | (8) |
| | | | | | | | 15 | 6.66 | -4 | | | | | " |
| | | | | | | | 25 | 1.37 | -4 | | | | | " |
| | | | | | | | 40 | 3.86 | -4 | 12.8 | 3.6 | 8 | | " |
| .36 | $m\text{-}NO_2C_6H_4COOC_2H_5 + OH^-$ | EW* | A = B = 0.05 | | | $k\,AB$ | 0 | 2.31 | -2 | | | | | (5) |
| | | | | | | | 15 | 8.15 | -2 | | | | | " |
| | | | | | | | 25 | 1.71 | -1 | | | | | " |
| | | | | | | | 40 | 4.88 | -1 | 12.8 | | | | " |
| .37 | $p\text{-}NO_2C_6H_4COOCH_3 + H_2O$ | Et85* | | - | - | $k\,AB$ | 25 | 4.29 | -2 | | | | | (1) |
| | | | | | | | 35 | 1.00 | -3 | 15.4 | | | | " |
| .38 | $p\text{-}NO_2C_6H_4COOCH_3 + H_2O$ | MW* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 100 | 1.65 | -4 | | | | | (7) |
| | | | | | | | 121 | 5.74 | -4 | | | | | " |
| | | | | | | | 138 | 1.54 | -3 | | | | | " |
| | | | | | | | 153 | 3.17 | -3 | 17.5 | 3.3 | 6 | | " |
| .39 | $p\text{-}NO_2C_6H_4COOCH_3 + OH^-$ | WA* | A = B = 0.05 | | | $k\,AB$ | 0 | 9.17 | -2 | | | | | (8) |
| | | | | | | | 15 | 3.11 | -2 | | | | | " |
| | | | | | | | 25 | 6.40 | -1 | | | | | " |
| | | | | | | | 40 | 1.70 | 0 | 12.3 | 6.92 | 8 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .40 | $p\text{-}NO_2C_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 80 | 2.86 | -5 | | | | | (7) |
| | | | | | | | 99 | 1.04 | -4 | | | | | " |
| | | | | | | | 119 | 3.32 | -4 | | | | | " |
| | | | | | | | 138 | 9.52 | -4 | 17.5 | 1.9 | 6 | | " |
| .41 | $p\text{-}NO_2C_6H_4COOC_2H_5 + OH^-$ | WA* | A = B = 0.05 | | - | $k\,AB$ | 0 | 3.58 | -2 | | | | | (8) |
| | | | | | | | 15 | 1.21 | -1 | | | | | " |
| | | | | | | | 25 | 2.44 | -1 | | | | | " |
| | | | | | | | 40 | 6.87 | -1 | 12.4 | 3.55 | 8 | | " |
| .42 | $o\text{-}F_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | - | $k\,AB$ | 25 | 6.45 | -4 | | | | (5) | (3) |
| | | | B = 0.005 | | | | 35 | 1.62 | -3 | 14.8 | | | | (1) |
| | | | | | | | 40 | 1.83 | -3 | 14.5 | 2.3 | 9 | | (3) |
| .43 | $o\text{-}FC_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | - | $k\,AB$ | 25 | 2.32 | -3 | | | | | (1) |
| | | | B = 0.005 | | | | 35 | 5.81 | -3 | | | | | " |
| | | | | | | | 50 | 2.10 | -2 | 16.9 | | | | " |
| .44 | $p\text{-}C_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | - | $k\,AB$ | 25 | 1.26 | -3 | | | | | (1) |
| | | | B = 0.005 | | | | 35 | 3.20 | -3 | | | | | " |
| | | | | | | | 50 | 1.20 | -2 | 17.2 | | | | " |
| .45 | $o\text{-}ClC_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | | $k\,AB$ | 25 | 1.39 | -3 | | | | | (1) |
| | | | B = 0,005 | | | | 35 | 3.38 | -2 | | | | | " |
| | | | | | | | 50 | 1.10 | -2 | 15.7 | | | | " |
| .46 | $m\text{-}ClC_6H_4COOC_2H_5 + OH^-$ | Et85* | | | | $k\,AB$ | 25 | 4.77 | -3 | | | | | (1) |
| | | | | | | | 35 | 1.18 | -2 | | | | | " |
| | | | | | | | 50 | 3.96 | -2 | 16.4 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .47 | $p$-$ClC_6H_4COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 80 | 1.85 | -5 | | | | | (7) |
| | | | | | | | 100 | 8.75 | -5 | | | | | " |
| | | | | | | | 120 | 3.55 | -4 | | | | | " |
| | | | | | | | 139 | 1.18 | -3 | 20.1 | 5.8 | 7 | | " |
| .48 | $p$-$ClC_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 80 | 1.86 | -5 | | | | | (7) |
| | | | | | | | 100 | 8.12 | -5 | | | | | " |
| | | | | | | | 121 | 3.12 | -4 | | | | | " |
| | | | | | | | 139 | 8.61 | -4 | 19.0 | 1 | 7 | | " |
| .49 | $p$-$ClC_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | | $k AB$ | 25 | 2.37 | -2 | | | | | (3) |
| | | | B = 0.005 | | | | 50 | 2.13 | -2 | 16.8 | 4.93 | 4 | | " |
| .50 | $p$-$BrC_6H_4COOC_2H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 60 | 3.4 | -6 | | | | | (7) |
| | | | | | | | 80 | 1.85 | -5 | | | | | " |
| | | | | | | | 100 | 8.64 | -5 | | | | | " |
| | | | | | | | 120 | 3.46 | -4 | | | | | " |
| | | | | | | | 139 | 1.11 | -3 | 20.1 | 5.2 | 7 | | " |
| .51 | $p$-$BrC_6H_4COOC_2H_5 + H_2O$ | EW* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 80 | 2.0 | -5 | | | | | (7) |
| | | | | | | | 100 | 8.62 | -5 | | | | | " |
| | | | | | | | 120 | 3.02 | -4 | | | | | " |
| | | | | | | | 139 | 9.55 | -4 | 18.9 | 1 | 9 | | " |
| .52 | $p$-$BrC_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | | $k AB$ | 25 | 2.89 | -3 | | | | | (3) |
| | | | B = 0.005 | | | | 50 | 2.60 | -2 | 16.8 | 5.82 | 9 | | " |
| .53 | $p$-$IC_6H_4COOC_2H_5 + OH^-$ | Et85* | A = 0.1 | | | $k AB$ | 25 | 2.78 | -3 | | | | | (3) |
| | | | B = 0.005 | | | | 50 | 2.48 | -2 | 16.7 | 4.9 | 9 | | " |

## SUPPLEMENTARY TABLE

(.6) $C_6H_5COOC_2H_5 + OH^-$ (2) ; $S^*$ = Solvent:

(I-VI) $H_2O$ 400 g + 1000 ml [$(CH_3)_2CO$ $x$ wt % + $C_2H_5OH$ $(1-x)$ wt %]

| | |
|---|---|
| (I) | $x$ = 100 |
| (II) | 88.95 |
| (III) | 75 |
| (IV) | 50.50 |
| (V) | 36.97 |
| (VI) | 25.04 |

(VII - XI) $H_2O$ + $C_2H_5OH$ $x$ wt %

| | |
|---|---|
| (VII) | $x$ = 47.9 |
| (VIII) | 66.5 |
| (IX) | 67.1 |
| (X) | 71.3 |
| (XI) | 93.5 |
| (XII) | 1,4-dioxane + $H_2O$ 400 g/l |

| °C | 0 | 16 | 25 | 39.7 | | $A = A^\circ \times 10^n$ | |
|---|---|---|---|---|---|---|---|
| $S^*$ | $10^4 k$ | | | | $E$ | $A^\circ$ | $n$ |
| (I) | 4.05 | 17.2 | 38.6 | 116.5 | 14.0 | 7.4 | 7 |
| (II) | 3.19 | 15.19 | 32.9 | 101.2 | 14.7 | 1.9 | 8 |
| (III) | 2.68 | 12.84 | 27.0 | 88.3 | 15.0 | 3.3 | 8 |
| (IV) | 2.17 | 10.78 | 24.02 | 77.6 | 15.2 | 3.9 | 8 |
| (V) | 1.79 | 9.49 | 21.4 | 73.3 | 15.8 | 9.1 | 8 |
| (VI) | 1.45 | 8.05 | 18.59 | 63.7 | 15.9 | 1 | 9 |
| (VII) | 1.78 | 9.20 | 21.05 | 68.4 | 15.6 | 6.6 | 8 |
| (VIII) | 1.29 | 6.54 | 15.3 | 55.5 | 16.0 | 1 | 9 |
| (IX) | 0.832 | 5.12 | 12.03 | 45.6 | 16.5 | 1.9 | 9 |
| (X) | 0.731 | 4.14 | 10.02 | 39.6 | 16.9 | 3.5 | 9 |
| (XI) | 0.183 | 1.17 | 3.56 | 15.57 | 19.0 | 3.5 | 10 |
| (XII) | 7.8 | 29.3 | 64.0 | 152.0 | 12.8 | 1.5 | 7 |

## SOLVENTS

| | |
|---|---|
| MW* | $CH_3OH + H_2O$ 40 ml/100 ml solution (5) (7) |
| WA* | $(CH_3)_2CO + H_2O$ 40 ml/100 ml solution (56 wt % $(CH_3)_2CO$) (7) (8) |
| EW* | $C_2H_5OH + H_2O$ 40 ml/100 ml solution (5) (7) |
| S* | See Supplementary Table (2) |
| Et85* | $C_2H_5OH$ 85 vol % + $H_2O$ 15 vol % (1) (3) |
| Et50* | $C_2H_5OH$ 50 vol % + $H_2O$ 50 vol % (6) |

## COMMENTS

(.7) (.42) At 25°, *k* of (1) averaged with the close value of (3).

## LITERATURE

(1) D.P. Evans, J.J. Gordon, H.B. Watson, *CSL* **1937**, 1430. (2) R.A. Fairclough, C.N. Hinshelwood, *CSL* **1937**, 538. (3) C.K. Ingold, W.S. Nathan, *CSL* **1936**, 222. (4) C.T. Lester, C.F. Bailye, *ACS* 1946, **68**, 375. (5) W.B.S. Newling, C.N. Hinshelwood, *CSL* **1936**, 1357. (6) W.H. Stevens, R.W. Attree, *CJR*$^B$ 1949, **27**, 807. (7) E.W. Timm, C.N. Hinshelwood, *CSL* **1938**, 862. (8) E. Tommila, C.N. Hinshelwood, *CSL* **1938**, 1801.

# ESTER SOLVOLYSIS

## Aliphatic carboxylic acid and Phenol



Reaction types

$$\underset{(A)}{RCOOAr} + \underset{(B)}{R'OH} \rightarrow \underset{(L)}{RCOOH} + \underset{(M)}{ArOR'}$$

$$\underset{(A)}{RCOOAr} + \underset{(B)}{OR'^{-}} \rightarrow \underset{(L)}{RCOO^{-}} + \underset{(M)}{ArOR'}$$

Rate measured (unless otherwise stated) $-dA/dt = +dM/dt$

All rates are in M/l per sec.
All amounts in M/l.
*Coded Solvents, Comments, Literature, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COOC_6H_5 + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 15 | 1.05 | -5 | | | | | (1) |
| | | | | | | | 25 | 2.70 | -5 | | | | | " |
| | | | | | | | 40 | 1.14 | -4 | | | | | " |
| | | | | | | | 60 | 5.81 | -4 | | | | | " |
| | | | | | | | 80 | 2.68 | -3 | 17.2 | 1.26 | 8 | | " |
| .2 | $CH_3COOC_6H_5 + OH^-$ | WA* | A = B = 0.05 | - | - | $k\,AB$ | -20 | 1.26 | -2 | | | | | (1) |
| | | | | | | | -12 | 2.53 | -2 | | | | | " |
| | | | | | | | 0 | 7.48 | -2 | | | | | " |
| | | | | | | | 15 | 2.50 | -1 | | | | | " |
| | | | | | | | 25 | 5.76 | -1 | 12.5 | 9.34 | 8 | | " |
| .3 | $CH_3COOC_6H_5 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \rightarrow$ | $H_2O$ + c wt % $C_2H_5OH$ | | HCl | 0.01 - 0.2 | $+ dM/dt = kA[H^+]$ $+ dL/dt = k'A[H^+]$ | | $k$ | | | | | | (2) |
| | $\begin{cases} (L)\ CH_3COOH \\ (L')\ CH_3COOC_2H_5 \end{cases} + C_6H_5OH\ (M)$ | c | | | | | | | | | | | | |
| | | 50 | | | | | 25 | 5.83 | -5 | | | | * | " |
| | | " | | | | | 40 | 2.18 | -4 | | | | | " |
| | | 70 | | | | | 25 | 5.53 | -5 | | | | | " |
| | | " | | | | | 40 | 2.10 | -4 | | | | | " |
| | | 95 | | | | | 25 | 1.83 | -4 | | | | | " |
| | | " | | | | | 35 | 2.58 | -4 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | *(continued)* $CH_3COOC_6H_5$ + $\begin{cases} H_2O \\ C_2H_5OH \end{cases}$ → | | | | | | | | $k'$ | | | | | |
| | | 50 | | | | | 25 | 4.0 | -5 | | | | * | (2) |
| | | " | | | | | 40 | 1.58 | -4 | | | | | " |
| | | 70 | | | | | 25 | 3.6 | -5 | | | | | " |
| | | " | | | | | 40 | 1.27 | -4 | | | | | " |
| | $\begin{cases} (L)\ CH_3COOH \\ (L')\ CH_3COOC_2H_5 \end{cases}$ + $C_6H_5OH$ (M) | 90 | | | | | 25 | 2.8 | -5 | | | | | " |
| | | " | | | | | 35 | 6.5 | -5 | | | | | " |
| .4 | $CH_3COO$ (m - $C_6H_4CH_3$) + $H_2O$ | WA* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 15 | 1.01 | -5 | | | | | (1) |
| | | | | | | | 25 | 2.66 | -5 | | | | | " |
| | | | | | | | 40 | 1.10 | -4 | | | | | " |
| | | | | | | | 60 | 5.75 | -4 | | | | | " |
| | | | | | | | 80 | 2.57 | -3 | 17.2 | 1.2 | 8 | | " |
| .5 | $CH_3COO$ (m - $C_6H_4CH_3$) + $OH^-$ | WA* | A = B = 0.05 | | - | $k AB$ | -20 | 8.2 | -3 | | | | | (1) |
| | | | | | | | -10 | 1.95 | -2 | | | | | " |
| | | | | | | | 0 | 5.22 | -2 | | | | | " |
| | | | | | | | 15 | 1.80 | -1 | | | | | " |
| | | | | | | | 25 | 3.80 | -1 | 12.9 | 1.1 | 9 | | " |
| .6 | $CH_3COO$ (p - $C_6H_4CH_3$) + $H_2O$ | WA* | 0.05 | HCl | 0.05 | $k A[H^+]$ | 25 | 2.93 | -5 | | | | | (1) |
| | | | | | | | 40 | 1.18 | -4 | | | | | " |
| | | | | | | | 60 | 6.19 | -4 | | | | | " |
| | | | | | | | 80 | 2.84 | -3 | 17.2 | 1.23 | 8 | | " |
| .7 | $CH_3COO$ (p - $C_6H_4CH_3$) + $OH^-$ | WA* | A = B = 0.05 | | - | $k AB$ | -20 | 6.5 | -3 | | | | | (1) |
| | | | | | | | -10 | 1.75 | -2 | | | | | " |
| | | | | | | | 0 | 4.50 | -2 | | | | | " |
| | | | | | | | 15 | 1.54 | -1 | | | | | " |
| | | | | | | | 25 | 3.10 | -1 | 12.9 | 9.78 | 8 | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .13 | $CH_3COO\ (m - C_6H_4NO_2) + H_2O$ | WA* | 0.05 | HCl | 0.05 | $k\,A[H^+]$ | 15 | 7.00 | -6 | | | | | (1) |
| | | | | | | | 20 | 1.94 | -5 | | | | | " |
| | | | | | | | 40 | 7.61 | -5 | | | | | " |
| | | | | | | | 60 | 3.79 | -4 | | | | | " |
| | | | | | | | 80 | 1.58 | -3 | 16.7 | 4.07 | 7 | | " |
| .14 | $CH_3COO\ (m - C_6H_4NO_2) + OH^-$ | WA* | A = B = 0.05 | | – | $k\,AB$ | -20 | 1.83 | -1 | | | | | (1) |
| | | | | | | | -10 | 4.10 | -1 | | | | | " |
| | | | | | | | 0 | 9.70 | -1 | | | | | " |
| | | | | | | | 15 | 2.80 | 0 | | | | | " |
| | | | | | | | 25 | 5.49 | 0 | 11.3 | 1.15 | 9 | * | " |
| .15 | $CH_3COO\ (p - C_6H_4NO_2) + OH^-$ | WA* | A = B = 0.05 | | – | $k\,AB$ | -20 | 2.90 | -1 | | | | | (1) |
| | | | | | | | -10 | 7.00 | -1 | | | | | " |
| | | | | | | | 0 | 1.40 | 0 | | | | | " |
| | | | | | | | 15 | 4.30 | 0 | | | | | " |
| | | | | | | | 25 | 8.05 | 0 | 11.0 | 1 | 9 | * | " |

## SOLVENTS

WA* $(CH_3)_2CO + H_2O$ 400 ml/l solution, (~ 56 wt % $(CH_3)_2CO$)

## COMMENTS

(.3) Selected data; $k'$ is from initial stage of the reaction. With increasing $c$, $k$ appears to pass through a minimum at about 60 - 70 %, then to increase; $k'$ decreases with increasing $c$. (.14) (.15) $k$ at 25°C extrapolated.

## LITERATURE

(1) E. Tomila, C.N. Hinshelwood, *CSL* **1938**, 1801. (2) W.A. Waters, *CSL* **1936**, 1014.

# ESTER SOLVOLYSIS

## Aliphatic carboxylic acid and Polyalcohol

*Liquid phase*

Amounts are in M/l.
Rates are in M/l sec.
Comments, Literature, at the end of the table.

Rate measured $-dB/dt = dM/dt$

$Ac = CH_3CO$

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $AcOCH_2CH_2OAc + 2OH^- \rightarrow OHCH_2CH_2OH + 2AcO^-$ | $H_2O$ | A = 0.005 - 0.25<br>B = 0.01 - 0.5 | $k$AB | 18<br>25 | 1.27<br>2.72 | -1<br>-1 |
| .2 | $AcOCH_2CH_2OAc + OH^- \rightarrow AcOCH_2CH_2OH + AcO^-$ | " | " | " | 18<br>25 | 2.70<br>5.28 | -1<br>-1 |
| .3 | $AcOCH_2CH_2OH + OH^- \rightarrow OHCH_2CH_2OH + AcO^-$ | " | " | " | 18<br>25 | 1.35<br>2.72 | -1<br>-1 |
| .4 | $AcOCH_2CH(OAc)CH_2OAc + 3OH^- \rightarrow OHCH_2CHOHCH_2OH + 3AcO^-$ | " | $10^3$A = 3.3 - 6.7<br>B = 0.1 - 0.2 | " | 18<br>25 | 1.32<br>2.89 | -1<br>-1 |
| .5 | $AcOCH_2CH(OAc)CH_2OAc + OH^- \rightarrow AcOCH_2CH(OAc)CH_2OH + AcO^-$ | " | " | " | 18<br>25 | 4.08<br>8.62 | -1<br>-1 |
| .6 | $AcOCH_2CHOHCH_2OAc + 2OH^- \rightarrow OHCH_2CHOHCH_2OH + 2AcO^-$ | " | A = 0.005 - 0.01<br>B = 0.1 - 0.2 | " | 18<br>25 | 1.31<br>2.97 | -1<br>-1 |
| .7 | $AcOCH_2CHOHCH_2OAc + OH^- \rightarrow AcOCH_2CHOHCH_2OH + AcO^-$ | " | $10^3$A = 3.3 - 6.7<br>B = 0.01 - 0.02 | " | 18<br>25 | 2.71<br>5.75 | -1<br>-1 |
| .8 | $OHCH_2CH(OAc)CH_2OH + OH^- \rightarrow OHCH_2CHOHCH_2OH + AcO^-$ | " | " | " | 18<br>25 | 1.35<br>2.87 | -1<br>-1 |

## COMMENTS

Reaction (.1) is composed of the two consecutive steps (.2) and (.3); with the subscripts referring to the reaction designated by that number, $k_1 \approx k_3$, and $k_2 = 2k_3$. Reaction (.4) is composed of the three consecutive steps (.5), (.7) and (.8); $k_4 \approx k_8$, $k_5 = 3k_8$ and $k_1 = 2k_8$. Reaction (.6) is composed of the two consecutive steps (.7) and (.8); $k_6 \approx k_8$, $k_7 = 2k_8$.

## LITERATURE

J. Meyer, *ZPC* 1909, 67, 257; E. Abel, *ZPC* 1906, 56, 558.

# ESTER SOLVOLYSIS

## Aliphatic carboxylic polyacid and Alcohol

Rate measured $-dB/dt = +dM/dt$

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.
Comments, Literature, at the end of the table

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $CH_3OCOCH_2CH_2COOCH_3 + 2OH^- \rightarrow {}^-OCOCH_2CH_2COO^- + 2CH_3OH$ | $H_2O$ | see Reactions (.2) (.3) | | | | |
| .2 | $CH_3OCOCH_2CH_2COOCH_3 + OH^- \rightarrow CH_3OCOCH_2CH_2COO^- + CH_3OH$ | " | 0.01 – 0.05 | $k$AB | 18 | 2.08 | −1 |
| | | | | | 25 | 3.42 | −1 |
| .3 | $CH_3OCOCH_2CH_2COO^- + OH^- \rightarrow {}^-OCOCH_2CH_2COO^- + CH_3OH$ | " | " | " | 18 | 2.17 | −2 |
| | | | | | 25 | 3.50 | −2 |
| .4 | $C_2H_5OCOCH_2CH_2COOC_2H_5 + 2OH^- \rightarrow {}^-OCOCH_2CH_2COO^- + 2C_2H_5OH$ | " | see Reactions (.5) (.6) | | | | |
| .5 | $C_2H_5OCOCH_2CH_2COOC_2H_5 + OH^- \rightarrow C_2H_5OCOCH_2CH_2COO^- + C_2H_5OH$ | " | 0.01 – 0.05 | $k$AB | 18 | 1.84 | −1 |
| | | | | | 25 | 2.84 | −1 |
| .6 | $C_2H_5OCOCH_2CH_2COO^- + OH^- \rightarrow OCOCH_2CH_2COO^- + C_2H_5OH$ | " | " | " | 18 | 1.72 | −2 |
| | | | | | 25 | 2.77 | −2 |
| .7 | $CH_3OCOCHOHCOOCH_3 + 2OH^- \rightarrow CHOH(COO^-)_2 + 2CH_3OH$ | " | see Reactions (.8) (.9) | | | | |
| .8 | $CH_3OCOCHOHCOOCH_3 + OH^- \rightarrow CH_3OCOCHOHCOO^- + CH_3OH$ | " | 0.01 – 0.05 | $k$AB | 18 | 1.45 | 0 |
| | | | | | 25 | 2.85 | 0 |
| .9 | $CH_3OCOCHOHCOO^- + OH^- \rightarrow CHOH(COO^-)_2 + CH_3OH$ | " | " | " | 18 | 1.75 | −2 |
| | | | | | 25 | 3.07 | −2 |



942151 O—51——11

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .10 | $C_2H_5OCOCHOHCOOC_2H_5 + 2OH^- \rightarrow CHOH(COO^-)_2 + 2C_2H_5OH$ | $H_2O$ | see Reactions (.11) (.12) | | | | |
| .11 | $C_2H_5OCOCHOHCOOC_2H_5 + OH^- \rightarrow C_2H_5OCOCHOHCOO^- + C_2H_5OH$ | " | 0.01 - 0.05 | $k$ AB | 18<br>25 | 1.04<br>2.25 | -1<br>-1 |
| .12 | $C_2H_5OCOCHOHCOO^- + OH^- \rightarrow CHOH(COO^-)_2 + C_2H_5OH$ | " | " | " | 18<br>25 | 1.40<br>2.44 | -2<br>-2 |

## COMMENTS

Reaction (.1) is composed of the consecutive steps (.2) and (.3). Reaction (.4) is composed of the consecutive steps (.5) and (.6). Reaction (.7) is composed of the consecutive steps (.8) and (.9). Reaction (.10) is composed of the consecutive steps (.11) and (.12). Rates of (.2), (.5), (.8), (.11), by extrapolation to zero time of, respectively, the rates of (.1), (.4), (.7), (.10).

## LITERATURE

J. Meyer, *ZPC* 1909, **67**, 257.

# SOLVOLYSIS

## Alkyl arylsulfonates

*Liquid phase*

Reaction type $ArSO_3R + OR'^- \rightarrow ROR' + ArSO_3^-$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5SO_3C_2H_5 + OC_2H_5^-$ | $C_2H_5OH$ | A = B = 0.05 | $k$AB | 35 | 1.28 | -3 | | | |
| | | | | | 45 | 3.92 | -3 | 21.7 | 6.0 | 10 |
| .2 | $p$-$CH_3C_6H_4SO_3C_2H_5 + OC_2H_5^-$ | $C_2H_5OH$ | A = B = 0.05 | $k$AB | 35 | 8.06 | -4 | | | |
| | | | | | 45 | 2.36 | -3 | 20.8 | 8.2 | 9 |
| .3 | $p$-$CH_3OC_6H_4SO_3C_2H_5 + OC_2H_5^-$ | $C_2H_5OH$ | A = B = 0.05 | $k$AB | 35 | 5.35 | -4 | | | |
| | | | | | 45 | 1.62 | -3 | 21.7 | 2.2 | 10 |
| .4 | $p$-$NO_2C_6H_4SO_3C_2H_5 + OC_2H_5^-$ | $C_2H_5OH$ | A = B = 0.05 | $k$AB | 25 | 3.85 | -3 | | | |
| | | | | | 35 | 1.50 | -2 | 24.0 | 3.0 | 13 |
| .5 | $p$-$BrC_6H_4SO_3C_2H_5 + OC_2H_5^-$ | $C_2H_5OH$ | A = B = 0.05 | $k$AB | 35 | 2.87 | -3 | | | |
| | | | | | 45 | 8.98 | -3 | 22.2 | 3.0 | 11 |

## LITERATURE

M.S.Morgan, L.M.Fletcher, *ACS* 1948, **70**, 375.

# SOLVOLYSIS

## Phenol sulfates

*Liquid phase*

Reaction type $ArOSO_3K + H_2O \rightarrow ArOH + KHSO_4$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 8.9 | -5 | |
| | | | | | | | 78.7 | 3.35 | -3 | 27.0 |
| .2 | $o$-$CH_3C_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 7.75 | -5 | |
| | | | | | | | 78.7 | 2.72 | -3 | 26.5 |
| .3 | $m$-$CH_3C_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 8.8 | -5 | |
| | | | | | | | 78.8 | 3.2 | -5 | 26.7 |
| .4 | $o$-$CH_3OC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 1.33 | -4 | |
| | | | | | | | 78.7 | 4.53 | -3 | |
| .5 | $m$-$CH_3OC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 1.02 | -4 | |
| | | | | | | | 78.7 | 3.4 | -3 | 26.1 |
| .6 | $p$-$CH_3OC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 4.5 | -5 | |
| | | | | | | | 78.7 | 1.80 | -5 | 27.4 |
| .7 | $o$-$NO_2C_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $k$A | 48.6 | 3.58 | -4 | |
| | | | | | | | 78.7 | 8.8 | -3 | 23.8 |

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $m\text{-}NO_2C_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $kA$ | 48.6 | 2.05 | -4 | |
| | | | | | | | 78.7 | 5.8 | -3 | 24.8 |
| .9 | $p\text{-}NO_2C_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $kA$ | 48.6 | 4.45 | -4 | |
| | | | | | | | 78.7 | 1.2 | -2 | 24.7 |
| .10 | $o\text{-}ClC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $kA$ | 48.6 | 1.30 | -4 | |
| | | | | | | | 78.7 | 4.42 | -3 | 26.2 |
| .11 | $m\text{-}ClC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $kA$ | 48.6 | 1.63 | -4 | |
| .12 | $p\text{-}ClC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $kA$ | 48.6 | 1.08 | -4 | |
| | | | | | | | 78.7 | 3.62 | -3 | 26.2 |
| .13 | $p\text{-}BrC_6H_4OSO_3K + H_2O$ | $H_2O$ | 0.08 | HCl | 0.04 | $kA$ | 48.6 | 1.15 | -4 | |

## LITERATURE

G.N.Burkhardt, W.G.K.Ford, E.Singleton, *CSL* **1936**, 17.

# ESTER SOLVOLYSIS

## Aliphatic alcohol and Hydrohalic acid

*Liquid phase*

Reaction types $RX + R'OH \rightarrow HX + ROR'$

(A) (B) (L) (M)

$RX + OR'^{-} \rightarrow X^{-} + ROR'$

Rate measured $-dA/dt = +dL/dt$
(unless otherwise stated)

Rates are in M/l per sec.

Amounts are in M/l.

Solvents, Comments, Literature, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Saturated alkyl halide** | | | | | | | | | | | |
| .1 | $CH_3Cl + H_2O$ | $H_2O$ | 0.1 | $k$ A | 25 | 3.32 | -10 | 27.7 | | | * | (21) |
| | | | | | 100 | 1.80 | -6 | 27.7 | | | | " |
| | | " | 0.033 | $k$ A | 37.8 | 1.27 | -7 | | | | | (21a) |
| | | | | | 60.0 | 2.16 | -6 | | | | | |
| .1.1 | $CH_3Cl + OH^-$ | $H_2O$ | A = 0.033; B = 0.099 | $k$ AB | 37.8 | 3.55 | -5 | | | | | (21a) |
| | | | | | 49.4 | 1.46 | -4 | | | | | |
| | | | | | 55.5 | 3.00 | -4 | | | | | |
| | | | | | 60.0 | 4.88 | -4 | | | | | |
| | | | | | 66.6 | 9. | -4 | 24.3 | 4.1 | 12 | | |
| .2 | $CH_3Br + H_2O$ | $H_2O$ | 0.1 | $k$ A | 25 | 6.00 | -9 | | | | * | (21) |
| | | | | | 100 | 2.09 | -5 | 26.5 | | | | |
| | | " | 0.063 | $k$ A | 24.5 | 3.21 | -7 | | | | | (21a) |
| | | | | | 35.4 | 1.46 | -6 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3Br + H_2O$ *(continued)* | EtOO | | – | – | $kA$ | 25 | 2.47 | -7 | | | | | ([28]) |
| | | | | | | | 55 | 8.32 | -6 | 22.8 | | | | " |
| | | EtOO | | – | – | " | 25 | 1.22 | -7 | | | | | " |
| | | | | | | | 55 | 5.86 | -6 | 23.7 | | | | " |
| | | $Me_2CO$ | B = 5 % | | | $kAB$ | 50 | 2.63 | -6 | | | | | ([29]) |
| | | | 10 % | | | | " | 4.31 | -8 | | | | | |
| | | PhOH | B = 0.5; L = 0.1; | | | $kAB$ | 80 | 9.56 | -6 | | | | | ([4]) |
| | | | M = 0.05 | | | | 92 | 3.19 | -5 | 26.6 | | | | |
| .2.1 | $CH_3Br + OH^-$ | $H_2O$ | A = 0.063; B = 0.105 | | | $kAB$ | 19.6 | 7.08 | -5 | | | | | ([21a]) |
| | | | | | | | 24.5 | 1.37 | -4 | | | | | |
| | | | | | | | 30.3 | 2.87 | -4 | | | | | |
| | | | | | | | 35.4 | 5.33 | -4 | | | | | |
| | | | | | | | 40.2 | 9.31 | -4 | | | | | |
| | | | | | | | 49.8 | 2.91 | -3 | 23.0 | 1.0 | 13 | | |
| | | EtOO | | | | $k_1A + k_2AB$ | 55 | | | | | | | ([16a]) |
| | | | | | | | $k_1$ | 3.49 | -6 | | | | | |
| | | | | | | | $k_2$ | 2.14 | -2 | | | | | |
| .3 | $CH_3I + H_2O$ | $H_2O$ | 0.1 | – | – | $kA$ | 25 | 1.14 | -9 | 28.1 | | | * | ([21]) |
| | | | | | | | 100 | 7.46 | -6 | 23.1 | | | | " |
| | | " | 0.012 | – | – | $kA$ | 69.7 | 2.45 | -5 | | | | | ([21a]) |
| .3.1 | $CH_3I + OH^-$ | $H_2O$ | A = 0.012; B = 0.104 | | | $kAB$ | 29.9 | 1.16 | -4 | | | | | ([21a]) |
| | | | | | | | 39.1 | 3.45 | -4 | | | | | |
| | | | | | | | 41.7 | 4.52 | -4 | | | | | |
| | | | | | | | 48.9 | 1.06 | -3 | | | | | |
| | | | | | | | 59.9 | 3.21 | -3 | | | | | |
| | | | | | | | 69.7 | 8.54 | -3 | 22.2 | 1.2 | 12 | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | $A = A^0 \times 10^n$ $A^0$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $C_2H_5Cl + OC_2H_5^-$ | EtOH | A = B = 0.05 | $k$AB | 40 | 1.1 | -5 | | | | * | ([10]) |
| | | | | | 60 | 9.9 | -5 | | | | | " |
| | | | | | 71 | 3.06 | -4 | | | | | " |
| | | | | | 80 | 7.73 | -4 | $7.93T^{1/2}$ | | 9 | | " |
| | | | | | 91 | 1.89 | -3 | 23.0 | | | | " |
| .5 | $C_2H_5Br + H_2O$ | EtOO | | $k$A | 25 | 1.01 | -7 | | | | | ([28]) |
| | | | | | 55 | 4.00 | -6 | 23.8 | | | | " |
| | | EtOO | | " | 25 | 5.06 | -8 | | | | | " |
| | | | | | 55 | 2.00 | -6 | 23.8 | | | | " |
| | | $(Me)_2CO$ | B = 5 % | $k$AB | 50 | 8.40 | -9 | | | | | ([29]) |
| | | | 10 % | | " | 1.45 | -8 | | | | | " |
| | | PhOH | B = 0.5; L = 0.1; | $k$AB | 80 | 2.69 | -6 | | | | | ([4]) |
| | | | M = 0.05 | | 92 | 1.28 | -5 | 31.3 | | | | " |
| .6 | $C_2H_5Br + OH^-$ | WAn | | $k$AB | 25 | 5.68 | -5 | | | | | ([8]) |
| | | | | | 40 | 2.66 | -4 | | | | | " |
| | | | | | 60 | 1.66 | -3 | | | | | " |
| | | | | | 80 | 8.01 | -3 | 18.5 | 2.5 | 9 | | " |
| | | WEt | | $k$AB | 25 | 4.71 | -5 | | | | | " |
| | | | | | 40 | 2.69 | -4 | | | | | " |
| | | | | | 60 | 2.02 | -3 | | | | | " |
| | | | | | 80 | 1.05 | -2 | 20.1 | 3.16 | 10 | | " |
| | | EtOO | | $k_1$A + $k_2$AB | 55 | | | | | | | ([16a]) |
| | | | | | $k_1$ | 1.39 | -6 | | | | | |
| | | | | | $k_2$ | 1.71 | -3 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6.1 | $C_2H_5Br + OC_2H_5^-$ | EtOH | A = 0.01 - 0.1 | | - | $k$AB | 16 | 2.37 | -5 | | | | * | ([10]) |
| | | | B = 0.01 - 0.1 | | | | 25 | 7.63 | -5 | | | | | " |
| | | | | | | | 32 | 1.83 | -4 | | | | | " |
| | | | | | | | 40 | 4.66 | -4 | | | | | " |
| | | | | | | | 50 | 1.35 | -3 | | | | | " |
| | | | | | | | 60 | 3.31 | -3 | | | | | " |
| | | | | | | | 71 | 1.02 | -2 | | | | | " |
| | | | | | | | 80 | 2.26 | -2 | 1.28 | $T^{1/2}$ | 10 | | " |
| | | | | | | | 90 | 5.28 | -2 | 21 | | | | " |
| | | | B = 0.0125 | | - | $k$AB | 60 | 4.3 | -3 | | | | | " |
| | | | 0.025 | | | | 60 | 3.7 | -3 | | | | | " |
| | | | 0.05 | | | | 60 | 3.2 | -3 | | | | | " |
| | | | 0.1 | | | | 60 | 2.8 | -3 | | | | | " |
| .7 | $C_2H_5I + H_2O$ | $H_2O$ | | - | - | $k$A | 60 | 1.67 | -5 | | | | | ([20]) |
| | | | | | | | 77 | 7.96 | -5 | | | | | " |
| | | | | | | | 100 | 5.13 | -4 | 21.2 | | | | " |
| .8 | $C_2H_5I + \begin{cases} H_2O & (=B) \\ C_2H_5OH & (=B') \end{cases} \longrightarrow HI + \begin{cases} C_2H_5OH & (a) \\ C_2H_5OC_2H_5 & (b) \end{cases}$ | | A = 0.01 - 0.17 | | (a + b)= | $k$A= | $k'$A(B + B') | | | | | | | ([7]) |
| | | $H_2O + C_2H_5OH$ % | | - | - | | 25 | | | | | | | " |
| | | | 18.4 | | | | $k$ | 1.17 | -7 | | | | | " |
| | | | " | | | | $k'$ | 2.87 | -9 | | | | | " |
| | | | 100 | | | | $k$ | 8.18 | -9 | | | | | " |
| | | | 100 | | | | $k'$ | 4.84 | -10 | | | | | " |
| | | | | | | | 50 | | | | | | | |
| | | | 18.4 | | | | $k$ | 3.83 | -6 | | | | | " |
| | | | " | | | | $k'$ | 8.17 | -9 | 26.0 | | | | " |
| | | | 55.5 | | | | $k$ | 1.38 | -6 | | | | | " |
| | | | " | | | | $k'$ | 4.17 | -9 | | | | | " |
| | | | 100 | | | | $k$ | 2.16 | -7 | | | | | " |
| | | | 100 | | | | $k'$ | 1.30 | -8 | 21.5 | | | | " |

| No. | Reaction | Medium (Solvent) | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .9 | $C_2H_5I + \begin{cases} H_2O \\ C_2H_5OH \\ (C_2H_5)_3N \ (=B) \end{cases} \rightarrow \begin{cases} HI + C_2H_5OH & (a) \\ HI + C_2H_5OC_2H_5 & (b) \\ (C_2H_5)_4NI & (c) \end{cases}$ | $H_2O + C_2H_5OH$ % | – | $(a + b + c) = k_1A + k_2AB = k'AB$ | | | | | | | | | (7) |
| | | | | | | 25 | | | | | | | " |
| | | 36.9 | | | | $k_2$ | 4.92 | -5 | | | | | " |
| | | " | | | | $k'$ | 5.14 | -5 | | | | | " |
| | | 55.5 | | | | $k_2$ | 2.08 | -5 | | | | | " |
| | | " | | | | $k'$ | 2.18 | -5 | | | | | " |
| | [See reaction (a + b), (.8)] | 100 | | | | $k_2$ | 2.67 | -6 | | | | | " |
| | | " | | | | $k'$ | 2.81 | -6 | | | | | " |
| | | | | | | 50 | | | | | | | |
| | | 18.1 | | | | $k_2$ | 6.18 | -4 | | | | | " |
| | | " | | | | $k'$ | 9.15 | -4 | | | | | " |
| | | 55.5 | | | | $k_2$ | 2.12 | -4 | | | | | " |
| | | " | | | | $k'$ | 2.40 | -4 | | | | | " |
| | | 100 | | | | $k_2$ | 3.83 | -5 | | | | | " |
| | | " | | | | $k'$ | 4.17 | -5 | | | | | " |
| .10 | $C_2H_5I + \begin{cases} H_2O \\ C_2H_5OH \\ CH_3COO^- \ (=B) \end{cases} \rightarrow \begin{cases} HI + C_2H_5OH & (a) \\ HI + C_2H_5OC_2H_5 & (b) \\ I^- + CH_3COOC_2H_5 & (c) \end{cases}$ | $H_2O + C_2H_5OH$ % | – | $(a + b + c) = k_1A + k_2AB = k'AB$ | | | | | | | | | (7) |
| | | | | | | 25 | | | | | | | " |
| | | 55.5 | | | | $k_2$ | 1.05 | -5 | | | | | " |
| | | " | | | | $k'$ | 1.50 | -5 | | | | | " |
| | | 100 | | | | $k_2$ | 1.00 | -5 | | | | | " |
| | [See reaction (a + b), (.8)] | " | | | | $k'$ | 1.17 | -5 | | | | | " |
| | | | | | | 50 | | | | | | | |
| | | 36.9 | | | | $k_2$ | 2.03 | -5 | | | | | " |
| | | " | | | | $k'$ | 4.18 | -5 | | | | | " |
| | | 55.5 | | | | $k_2$ | 1.87 | -5 | | | | | " |
| | | " | | | | $k'$ | 3.16 | -5 | 22.0 | | | | " |
| | | 75.8 | | | | $k_2$ | 2.47 | -5 | | | | | " |
| | | " | | | | $k'$ | 4.16 | -5 | | | | | " |
| | | 100 | | | | $k_2$ | 2.05 | -5 | | | | | " |
| | | " | | | | $k'$ | 2.50 | -5 | 23.2 | | | | " |

| No | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $C_2H_5I + \left\{\begin{matrix} H_2O \\ C_2H_5OH \\ OH^- \\ OC_2H_5^- \end{matrix}\right\}$ (=B) $\rightarrow$ $HI + \left\{\begin{matrix} C_2H_5OH & (a) \\ C_2H_5OC_2H_5 & (b) \end{matrix}\right.$ ; $I^- + \left\{\begin{matrix} C_2H_5OH \\ C_2H_5OC_2H_5 \end{matrix}\right\}$ (c) | | A = 0.06 - 0.15 | | (a + b + c) = $k_1A + k_2AB = k'AB$ | | | | | | | | | (7) |
| | | | B = 0.007 - 0.5 | | | | | | | | | | | " |
| | | $H_2O + C_2H_5OH$ % | | | | | 25 | | | | | | | " |
| | | | 36.9 | | | | $k_2$ | 5.33 | -5 | | | | | " |
| | | | " | | | | $k'$ | 5.68 | -5 | | | | | " |
| | | | 66.3 | | | | $k_2 = k'$ | 7.67 | -5 | | | | | " |
| | | | 100 | | | | " | 1.03 | -4 | | | | | " |
| | [See reaction (a + b), (.8)] | | | | | | 50 | | | | | | | |
| | | | 18.1 | | | | $k_2 = k'$ | 3.76 | -4 | | | | | " |
| | | | 36.9 | | | | " | 7.50 | -4 | 19.8 | | | | " |
| | | | 55.5 | | | | " | 8.25 | -4 | 18.8 | | | | " |
| | | | 75.4 | | | | " | 1.35 | -3 | 20.7 | | | | " |
| | | | 100 | | | | " | 1.38 | -3 | 19.8 | | | | " |
| .12 | $C_2H_5I + OC_2H_5^-$ | EtOH | A = B = 0.05 | | - | $k$ AB | 16 | 5.03 | -5 | | | | * | (10) |
| | | | | | | | 25 | 1.53 | -4 | | | | | " |
| | | | | | | | 32 | 3.68 | -4 | | | | | " |
| | | | | | | | 40 | 9.58 | -4 | | | | | " |
| | | | | | | | 50 | 2.70 | -3 | | | | | " |
| | | | | | | | 60 | 6.71 | -3 | | | | | " |
| | | | | | | | 71 | 1.99 | -2 | | | | | " |
| | | | | | | | 80 | 4.60 | -2 | 2.70 | $T^{1/2}$ | 10 | | " |
| | | | | | | | 91 | 1.19 | -1 | 21.0 | | | | " |
| .13 | $C_3H_7Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | | | | | | | | | |
| | | | | | | $k$ AB | 80 | 2.02 | -6 | | | | | (4) |
| | | | | | | | 92 | 9.50 | -6 | 31.7 | | | | " |
| .14 | $(CH_3)_2CHCl + H_2O$ | EtSO | 0.1 | - | - | $k$ A | 90 | 2.21 | -7 | | | | | (15) |
| | | | | | | | 110 | 1.15 | -6 | | | | | " |
| .15 | $(CH_3)_2CHCl + OH^-$ | EtSO | | - | - | $k$ AB | 70 | 5.08 | -6 | | | | | (15) |
| | | | | | | | 90 | 3.27 | -5 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .16 | $(CH_3)_2CHBr + H_2O$ | Et$_2$O | | – | – | $k$A | 25 | 2.64 | −7 | | | | | (28) |
| | | | | | | | 55 | 7.13 | −6 | 22.7 | | | | " |
| | | Et$_2$O | | – | – | $k$A | 25 | 7.84 | −8 | | | | | " |
| | | | | | | | 55 | 2.37 | 6 | 23.2 | | | | " |
| | | (Me)$_2$CO | B = 5 % | – | – | $k$AB | 50 | 1.34 | −8 | | | | | (29) |
| | | | 10 % | | | | " | 2.03 | −8 | | | | | " |
| .17 | $(CH_3)_2CHBr + OH^- \longrightarrow Br^- + (CH_3)_2CHOH$ | Et$_2$O | A = 0.1; | B = 0–0.005 | | $k$A | 45 | 2.23 | −6 | | | | * | (13) |
| | | | | | | | 55 | 6.67 | −6 | | | | | " |
| | | | | | | | 65 | 1.87 | −5 | | | | | " |
| | | | | | | | 75 | 4.92 | −5 | 22.7 | | | | " |
| | | Et$_2$O | A = 0.1; | B = 0.85 | | $k$AB | 45 | 1.38 | −5 | | | | | " |
| | | | | | | | 60 | 6.00 | −5 | | | | | " |
| | | | | | | | 75 | 2.35 | −4 | 20.7 | | | | " |
| | | Et$_2$O | A = 0.1; | B = 0–0.005 | | $k$A | 45 | 7.70 | −7 | | | | | " |
| | | | | | | | 55 | 2.38 | −6 | | | | | " |
| | | | | | | | 65 | 6.81 | −6 | | | | | " |
| | | | | | | | 75 | 1.81 | −5 | 23.2 | | | | " |
| | | Et$_2$O | A = 0.1; | B = 0.85 | – | $k$AB | 50 | 2.80 | −5 | | | | | " |
| | | | | | | | 80 | 4.98 | −4 | 21.7 | | | | " |
| | | EtOH | | | $k$A + $k_2$AB | | 55 | | | | | | | (16a) |
| | | | | | | | $k_1$ | 2.37 | −6 | | | | | |
| | | | | | | | $k_2$ | 4.75 | −5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .18 | $(CH_3)_2CHBr + OH^- \longrightarrow Br^- + \begin{cases} (CH_3)_2CHOH & (a) \\ CH_3CH{:}CH_2 + H_2O & (b) \end{cases}$ | Et60 | A = 0.1; B = 0.85 | | | | | | | | | | | |
| | | | | | (a + b) = | $k$AB | 45 | 2.94 | -5 | | | | | ([13]) |
| | | | " | " | | | 60 | 1.35 | -4 | | | | | " |
| | | | " | " | | | 75 | 5.55 | -4 | 21.5 | | | | " |
| | [See reaction (a), (.17)] | | " | 0.1 | | " | 45 | 5.08 | -5 | | | | | " |
| | | | " | 0.2 | | | " | 4.70 | -5 | | | | | " |
| | (See Supplementary table) | | " | 0.5 | | | " | 3.72 | -5 | | | | | " |
| | | | " | 1.0 | | | " | 2.94 | -5 | | | | | " |
| | | Et80 | A = 0.1; B = 0.85 | | | " | 50 | 6.70 | -5 | | | | | " |
| | | | | | | | 80 | 1.28 | -3 | 22.2 | | | | " |
| .19 | $(CH_3)_2CHI + H_2O$ | Et60 | 0.1 | - | - | $k$A | 50 | 4.94 | -6 | | | | | ([15]) |
| | | | | | | | 60 | 4.26 | -5 | | | | | " |
| .20 | $(CH_3)_2CHI + OH^-$ | Et60 | | - | - | $k$AB | 70 | 5.08 | -6 | | | | | ([15]) |
| | | | | | | | 90 | 3.28 | -5 | | | | | " |
| .21 | $C_4H_9Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | | | | | | | | | |
| | | | | | | $k$AB | 80 | 2.17 | -6 | | | | | ([4]) |
| | | | | | | | 92 | 8.16 | -6 | 29.6 | | | | " |
| .22 | $(CH_3)_2CHCH_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | | | | | | | | | |
| | | | | | | $k$AB | 80 | 9.32 | -7 | | | | | ([4]) |
| | | | | | | | 92 | 2.07 | -6 | 28.4 | | | | " |
| .22.1 | $(CH_3)_2CHCH_2Br + OC_2H_5^-$ | $C_2H_5OH$ | | | | $k$AB | 55 | 5.8 | -2 | | | | | ([16a]) |
| .23 | $(C_2H_5)(CH_3)CHBr + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | | | | | | | | | |
| | | | | | | $k$AB | 80 | 1.58 | -5 | | | | | ([4]) |
| | | | | | | | 92 | 5.84 | -5 | 29.9 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .24 | $(CH_3)_3CCl + \begin{cases} H_2O \\ CH_3OH \end{cases} \rightarrow \begin{cases} HCl + (CH_3)_3COH & (a) \\ HCl + (CH_3)_3COCH_3 \\ CH_3Cl + (CH_3)_3COH \end{cases} (b)$ | MeOH | | - | (a + b) = | $kA$ | 25 | 8.20 | -7 | | | | * | (11) |
| | | MeOH + $H_2O$ (N) | | | | | | | | | | | | " |
| | | | 0.070 | | | | " | 1.75 | -6 | | | | | " |
| | | | 0.175 | | | | " | 4.33 | -6 | | | | | " |
| | | | 0.230 | | | | " | 7.14 | -6 | | | | | " |
| | | | 0.282 | | | | " | 1.13 | -5 | | | | | " |
| | (See Supplementary table) | | 0.346 | | | | " | 2.12 | -5 | | | | | " |
| | | | 0.432 | | | | " | 5.28 | -5 | | | | | " |
| | | | 0.497 | | | | " | 9.75 | -5 | | | | | " |
| | | $H_2O$ | 1.000 | | | | " | 3.3 | -2 | | | | | " |
| .25 | $(CH_3)_3CCl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \rightarrow \begin{cases} HCl + (CH_3)_3COH & (a) \\ HCl + (CH_3)_3COC_2H_5 \\ C_2H_5Cl + (CH_3)_3COH \end{cases} (b)$ | EtOH %, $H_2O$ (N) | | - | (a + b) = | $kA$ | | | | | | | (32) | (11) |
| | | 100 | 0.000 | | | | 25 | 9.70 | -8 | | | | * | " |
| | | 90 | 0.262 | | | | " | 1.73 | -6 | | | | | " |
| | | 80 | 0.448 | | | | " | 9.24 | -6 | | | | | " |
| | (See Supplementary table) | 70 | 0.582 | | | | " | 4.07 | -5 | | | | | " |
| | | 60 | 0.684 | | | | " | 1.27 | -4 | | | | | " |
| | | 50 | 0.765 | | | | " | 3.67 | -4 | | | | | " |
| | | 40 | 0.829 | | | | " | 1.29 | -3 | | | | | " |
| | | 0 | 1.000 | | | | " | 3.3 | -2 | | | | | " |
| .26 | $(CH_3)_3CCl + H_2O$ | $H_2O$ + EtOH % | | | | | | | | | | | | |
| | | 40 | 0.05-0.08 | $OH^-$ | < A | $kA$ | 25 | 1.29 | -3 | | | | * | (12) |
| | | 50 | " | " | " | " | 8 | 3.53 | -5 | | | | | " |
| | | | | | | | 16 | 1.10 | -4 | | | | | " |
| | | | | | | | 25 | 3.67 | -4 | 22.9 | 2.8 | 13 | | " |
| | | 70 | " | " | " | " | 25 | 4.03 | -4 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .26 | $(CH_3)_3CCl + H_2O$ *(continued)* | 80 | 0.05-0.08 | $OH^-$ | < A | $k$A | 8 | 8.62 | -7 | | | | | (12) |
| | | | | | | | 16 | 2.72 | -6 | | | | | " |
| | | | | | | | 35 | 3.15 | -5 | | | | | " |
| | | | | | | | 45 | 1.04 | -4 | 23.1 | 6.9 | 11 | | " |
| | | EtOH | | | | $k$A | 25 | 8.54 | -6 | | | | | (16a) |
| | | An80 | 0.05-0.08 | $OH^-$ | < A | $k$A | 35 | 6.61 | -6 | | | | * | (12) |
| | | | | | | | 45 | 2.12 | -5 | 22.9 | 7.8 | 10 | | " |
| .27 | $(CH_3)_3CBr + H_2O$ | Et80 | | - | - | $k$A | 15 | 1.17 | -3 | | | | | (28) |
| | | | | | | | 25 | 3.20 | -3 | 17.2 | | | | " |
| | | Et80 | | - | - | " | 15 | 1.02 | -4 | | | | | " |
| | | | | | | | 25 | 3.31 | -4 | 20.0 | | | | " |
| | | $(Me)_2CO$ | B = 5 % | | - | $k$AB | 50 | 1.67 | -5 | | | | | (29) |
| | | | 10% | | | | " | 5.12 | -5 | | | | | " |
| .28 | $(CH_3)_3CBr + OH^-$ | Et80 | | | | $k$AB | 55 | 1.0 | -2 | | | | | (16a) |
| .29 | $C_5H_{11}Br + H_2O$ | An50 | 0.01 | | | $k$A | 50 | 7.7 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 2.2 | -6 | 22.1 | 5.2 | 8 | | |
| | | " | " | KOH | 0.05 | $k$A | 50 | 5.8 | -6 | | | | | " |
| | | | | | " | | 60 | 1.5 | -5 | | | | | |
| | | | | | 0.10 | | 50 | 1.0 | -5 | | | | | |
| | | | | | " | | 60 | 2.7 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 2.0 | -5 | | | | | |
| | | | | | " | | 60 | 4.9 | -5 | | | | | |
| .30 | $C_5H_{11}Br + H_2O$ | PhOH | B = 0.5; | L = 0.1; | M = 0.05 | | | | | | | | | |
| | | | | | | $k$AB | 80 | 2.47 | -6 | | | | | (4) |
| | | | | | | | 92 | 8.28 | -6 | 30.6 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .31 | $(CH_3)_2CH(CH_2)_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | | | | | | | | | |
| | | | | | | $kAB$ | 80 | 9.00 | −6 | | | | | (4) |
| | | | | | | | 92 | 3.60 | −5 | 30.1 | | | | " |
| .31.1 | $C_2H_5C(CH_3)_2Cl + H_2O$ | Et80 | | | | $kA$ | 25 | 1.50 | −5 | | | | | (16a) |
| .32 | $C_2H_5C(CH_3)_2Cl + OH^-$ | Et80 | B = 0.212; A = 0.073 | | | $kA$ | 25.2 | 1.1 | −4 | | | | * | (14a) |
| | | Et80 | B = 0.212; A = 0.161 | | | $kA$ | 25.2 | 9.4 | −6 | | | | " | " |
| | | | | | 0.078 | | " | 1.0 | −5 | | | | | |
| | | | | | 0.147 | | 50.0 | 1.7 | −4 | | | | | |
| .33 | $C_2H_5C(CH_3)_2Br + OH^-$ | Et80 | B = 0.118; A = 0.072 | | | $kA$ | 25.2 | 4.3 | −4 | | | | * | " |
| | | | | | 0.005 | | | 4.0 | −4 | | | | | |
| .33.1 | $(CH_3)_3CCH_2Br + OC_2H_5^-$ | $C_2H_5OH$ | | | | $kAB$ | 95 | 5.0 | −4 | | | | | (16a) |
| .34 | $CH_3N(CH_2CH_2Cl)_2 + 2\ OH^-$ | D1W | A = B = 0.01 − 0.05 | | | $kA$ | 25.0 | 3.0 | −4 | | | | * | (2b) |
| .35 | $CH_3N(CH_2CH_2Cl)_2 + H_2O$ | D1W | See Comments | | | | | | | | | | * | (2b) |
| .36 | $C_2H_5N(CH_2CH_2Cl)_2 + H_2O$ | D1W | See Comments | | | | | | | | | | * | (2a) |
| .37 | $C_6H_{13}Cl + H_2O$ | An50 | 0.01 | | | $kA$ | 50 | 2.2 | −8 | | | | * | (22b) |
| | | | | | | | 60 | 6.7 | −8 | | | | | |
| | | " | " | KOH | 0.05 | $kA$ | 50 | 1.5 | −7 | | | | | " |
| | | | | | " | | 60 | 4.3 | −7 | | | | | |
| | | | | | 0.10 | | 50 | 2.7 | −7 | | | | | |
| | | | | | " | | 60 | 7.7 | −7 | | | | | |
| | | | | | 0.25 | | 50 | 4.5 | −7 | | | | | |
| | | | | | " | | 60 | 1.5 | −6 | | | | | |



942151 O—51——12

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .38 | $C_6H_{13}Br + H_2O$ | An50 | 0.01 | | | $k$ A | 50 | 7.0 | -7 | | | | * | ([22b]) |
| | | | | | | | 60 | 2.0 | -6 | 22.6 | 1.1 | 9 | | |
| | | " | " | KOH | 0.05 | $k$ A | 50 | 5.2 | -6 | | | | | " |
| | | | | | " | | 60 | 1.35 | -5 | | | | | |
| | | | | | 0.10 | | 50 | 9.2 | -6 | | | | | |
| | | | | | " | | 60 | 2.3 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 1.7 | -5 | | | | | |
| | | | | | " | | 60 | 4.4 | -5 | | | | | |
| | | AnD50 | | | | $k$ A | 50 | 5.8 | -7 | | | | | " |
| | | | | | | | 60 | 1.6 | -6 | | | | | |
| .39 | $C_6H_{13}Br + H_2O$ | PLOH | B = 0.5; L = 0.1; M = 0.05 | | | | | | | | | | | |
| | | | | | | $k$ AB | 80 | 1.96 | -6 | | | | | ([4]) |
| | | | | | | | 92 | 8.18 | -5 | 30.9 | | | | " |
| .40 | $(CH_3)_2CHCH_2CH_2CH_2Br + H_2O$ | An50 | 0.01 | | | $k$ A | 50 | 7.3 | -7 | | | | * | ([22b]) |
| | | | | | | | 60 | 2.1 | -6 | 22.3 | 7.5 | 8 | | |
| | | " | " | KOH | 0.05 | $k$ A | 50 | 5.5 | -6 | | | | | " |
| | | | | | " | | 60 | 1.35 | -5 | | | | | |
| | | | | | 0.10 | | 50 | 9.0 | -6 | | | | | |
| | | | | | " | | 60 | 2.4 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 1.7 | -5 | | | | | |
| | | | | | " | | 60 | 4.5 | -5 | | | | | |
| .41 | $C_2H_5CH(CH_3)CH_2CH_2Br + H_2O$ | An50 | 0.01 | | | $k$ A | 50 | 5.0 | -7 | | | | * | ([22b]) |
| | | | | | | | 60 | 1.4 | -6 | 21.75 | 2.1 | 8 | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .41 | $C_2H_5CH(CH_3)CH_2CH_2Br + H_2O$ *(continued)* | An50 | 0.01 | KOH | 0.05 | $kA$ | 50 | 1.5 | -6 | | | | | (22b) |
| | | | | | " | | 60 | 8.9 | -6 | | | | | |
| | | | | | 0.10 | | 50 | 6.0 | -6 | | | | | |
| | | | | | " | | 60 | 1.6 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 1.1 | -5 | | | | | |
| | | | | | " | | 60 | 2.8 | -5 | | | | | |
| .42 | $C_7H_{15}Br + H_2O$ | An50 | 0.01 | | | $kA$ | 50 | 6.6 | -7 | | | | | (22b) |
| | | | | | | | 60 | 1.85 | -6 | 22.1 | 4.7 | 8 | | |
| | | " | " | KOH | 0.05 | $kA$ | 50 | 4.8 | -6 | | | | | " |
| | | | | | " | | 60 | 1.2 | -5 | | | | | |
| | | | | | 0.10 | | 50 | 8.5 | -6 | | | | | |
| | | | | | " | | 60 | 2.1 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 1.5 | -5 | | | | | |
| | | | | | " | | 60 | 4.1 | -5 | | | | | |
| .43 | $C_7H_{15}Br + H_2O$ | PhOH | B = 0.5; | L = 0.1; | M = 0.05 | $kAB$ | 80 | 3.02 | -6 | | | | | (4) |
| | | | | | | | 92 | 1.12 | -5 | 30.1 | | | | " |
| .44 | $C_5H_{11}CH(CH_3)Br + H_2O$ | An50 | 0.01 | | | $kA$ | 50 | 3.7 | -6 | | | | * | (22b) |
| | | | | | | | 60 | 1.0 | -5 | 21.9 | 2.0 | 9 | | |
| | | " | " | KOH | 0.05 | $kA$ | 50 | 7.7 | -6 | | | | | " |
| | | | | | " | | 60 | 2.1 | -5 | | | | | |
| | | | | | 0.10 | | 50 | 1.1 | -5 | | | | | |
| | | | | | " | | 60 | 2.8 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 1.7 | -5 | | | | | |
| | | | | | " | | 60 | 4.5 | -5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .45 | $C_8H_{17}Br + H_2O$ | An50 | 0.01 | | | $kA$ | 50 | 6.3 | -7 | | | | | (22b) |
| | | | | | | | 60 | 1.8 | -6 | 22.2 | 5.1 | 8 | | |
| | | " | " | KOH | 0.05 | $kA$ | 50 | 4.6 | -6 | | | | | " |
| | | | | | " | | 60 | 1.15 | -5 | | | | | |
| | | | | | 0.10 | | 50 | 7.9 | -6 | | | | | |
| | | | | | " | | 60 | 2.0 | -5 | | | | | |
| | | | | | 0.25 | | 50 | 1.45 | -5 | | | | | |
| | | | | | " | | 60 | 3.6 | -5 | | | | | |
| .46 | $C_8H_{17}Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $kAB$ | 80 | 2.36 | -6 | | | | | (4) |
| | | | | | | | 92 | 8.90 | -6 | 29.5 | | | | " |
| .47 | $C_6H_{13}CH(CH_3)Cl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow HCl + \begin{cases} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \\ C_8H_{16} + H_2O & (c) \end{cases}$ | Et60 | 0.057 | (a + b + c) = | | $kA$ | 100 | 8.05 | -6 | | | | * | (14) |
| | | | See following reaction (a + b) | | | | | | | | | | | |
| .48 | $C_6H_{13}CH(CH_3)Cl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow HCl + \begin{cases} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \end{cases}$ | Et60 | 0.057 | - | (a + b) = | $kA$ | 100 | 7.00 | -6 | | | | | (14) |
| .49 | $C_6H_{13}CH(CH_3)Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow HBr + \begin{cases} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \\ C_8H_{16} + H_2O & (c) \end{cases}$ | Et60 | 0.057 | (a + b + c) = | | $kA$ | 80 | 5.18 | -5 | | | | (14) | (16) |
| | | | | | | | 100 | 2.86 | -4 | 22 | | | * | " |
| | | | See following reaction (a + b) | | | | | | | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .50 | $C_6H_{13}CH(CH_3)Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow HBr + \begin{cases} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \end{cases}$ | Et60 | 0.057 | - | (a + b) = | $kA$ | 80 | 4.66 | -5 | | | | | (14) (16) |
| | | | | | | | 100 | 2.30 | -4 | | | | | " |
| .51 | $C_6H_{13}CH(CH_3)Br + \begin{cases} OH^- \\ OC_2H_5^- \end{cases} \longrightarrow Br^- + \begin{cases} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \\ C_8H_{16} + H_2O \end{cases}$ | Et60 | A = 0.057<br>B = 0.80 | (a + b + c) = | | $kAB$ | 80 | 7.96 | -4 | | | | * | (14) (16) |
| | | | See following reaction (a + b) | | | | | | | | | | | |
| .52 | $C_6H_{13}CH(CH_3)Br + \begin{cases} OH^- \\ OC_2H_5^- \end{cases} \longrightarrow Br^- + \begin{cases} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \end{cases}$ | Et60 | A = 0.057<br>B = 0.80 | - | (a + b) = | $kAB$ | 80 | 3.56 | -4 | | | | | (14) (16) |
| .52.1 | $(CH_3)_3C.C(C_2H_5)_2Cl + H_2O$ | Et80 | | | | $kA$ | 25 | 1.17 | -4 | | | | | (16a) |
| | **Carboxyl - substituted alkyl** | | | | | | | | | | | | | |
| .53 | $CH_2(COO^-)Cl + H_2O$ | $H_2O$ | 0.2 | $NaNO_3$ | 1 - A | $kA$ | 25 | 2.75 | -8 | | | | * | (6) |
| .54 | $CH_2(COO^-)Cl + H_2O \rightarrow CH(COO^-)(OH_3^+) + Br^-$ | $H_2O$ | 0.2 | $NaNO_3$ | 1 - A | $kAB$ | 25 | 5.0 | -10 | | | | * | (5) (25) |
| .55 | $CH_2(COO^-)Br + H_2O$ | $H_2O$ | 0.2 | $NaNO_3$ | 1 - A | $kA$ | 25 | 5.40 | -8 | | | | * | (6) |
| .56 | $CH_2(COO^-)Br + H_2O \rightarrow CH(COO^-)(OH_3^+) + Br^-$ | $H_2O$ | 0.2 | $NaNO_3$ | 1 - A | $kAB$ | 25 | 1.0 | -9 | | | | * | (5) (25) |
| .57 | $CH_2(COO^-)Br + OH^-$ | $H_2O$ | A = 0.05 - 0.5<br>B = 0 - 0.7<br>$NaNO_3$ = 1 - (A + B) | | | $kAB$ | 25 | 6.9 | -5 | | | | | (5) (25) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Halogen - substituted alkyl** | | | | | | | | | | | | | |
| .58 | $BrCH_2CH_2Br + H_2O$ | An25 | 0.01 | | | $kA$ | 60 | 1.7 | -7 | | | | * | (22b) |
| | | " | " | KOH | 0.375 | $kA$ | 30 | 7.8 | -5 | | | | | " |
| | | | | | | | 60 | fast | | | | | | |
| .59 | $CH_3CHBr_2 + H_2O$ | An25 | 0.01 | | | $kA$ | 60 | 4.3 | -8 | | | | * | (22b) |
| | | " | " | KOH | 0.375 | $kA$ | 30 | 3.8 | -7 | | | | * | " |
| | | | | | | | 60 | 1.35 | -5 | | | | | |
| .60 | $ClCH_2CH_2CH_2Br + H_2O$ | PhOH | | | | $kAB$ | 97 | 2.81 | -6 | 26.6 | | | | (4) |
| | | | B = 0.5; | L = 0.1; | M = 0.05 | | | | | | | | | |
| .61 | $ClCH_2CH_2CH_2CH_2Br + H_2O$ | PhOH | | | | $kAB$ | 97 | 6.40 | -6 | 26.6 | | | | (4) |
| | | | B = 0.5; | L = 0.1; | M = 0.05 | | | | | | | | | |
| | **Unsaturated alkenyl halide** | | | | | | | | | | | | | |
| .62 | $CH_2{:}CHCH_2CH_2Cl + H_2O$ | Et50 | 0.1 | - | - | $kA$ | 25 | 1.48 | -6 | | | | | (33) |
| .63 | $CH_2{:}CHCH_2CH_2Cl + OH^-$ | Et50 | A = 0.1; | B = | | $k_1A + k_2AB$ | 25 | | | | | | | (33) |
| | | | | 0.00 | | | $k_1$ | 1.48 | -6 | | | | | " |
| | | | | " | | | $k_2$ | 0 | | | | | | " |
| | | | | 0.05 | | | $k_1$ | 1.42 | -6 | | | | | " |
| | | | | " | | | $k_2$ | 3.08 | -4 | | | | | " |
| | | | | 0.1 | | | $k_1$ | 1.33 | -6 | | | | | " |
| | | | | " | | | $k_2$ | 2.92 | -4 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .63 | $CH_2{:}CHCH_2CH_2Cl + OH^-$ *(continued)* | Et50 | A = 0.2; B = 0.27 | | | $k$AB | 25 | 5.61 | -5 | | | | * | ([33]) |
| .64 | $CH_2{:}CHCH(CH_3)Cl + H_2O \rightarrow HCl + \begin{cases} CH_2{:}CHCH(CH_3)OH & (a) \\ OHCH_2CH{:}CH(CH_3) & (b) \end{cases}$ | Et50 | 0.13 | - | (a + b) = | $k$A | 25 | 1.14 | -5 | | | | | ([33]) |
| .65 | $CH_2{:}CHCH(CH_3)Cl + OH^- \rightarrow Cl^- + \begin{cases} CH_2{:}CHCH(CH_3)OH & (a) \\ OHCH_2CH{:}CH(CH_3) & (b) \end{cases}$ | Et50 | A = 0.07 - 0.13; | | (a + b) = | $k$A | | | | | | | * | ([33]) |
| | | | B = 0.00 | | | " | 25 | 1.14 | -5 | | | | | " |
| | | | 0.05 | | | | " | 1.21 | -5 | | | | | " |
| | | | 0.2 | | | | " | 1.28 | -5 | | | | | " |
| | | | A = 0.2; B = 0.2 | | (a + b) = | $k$AB | 25 | 1.01 | -6 | | | | * | " |
| | | | " | | | | 40 | 6.25 | -6 | | | | | " |
| | | | 0.1 | | | | " | 7.56 | -6 | | | | | " |
| .66 | $CH_3CHClCH{:}CHCl + H_2O$ | Et50 | 0.08 | | | $k$A | 25 | 1.1 | -4 | | | | | ([01]) |
| .67 | $CH_3CHClCH{:}CHCl + OC_2H_5^-$ | EtOH abs. | A = 0.08; B = 0.1 - 0.4 | | | $k$AB | 25 | 4.1 | -6 | | | | | ([01]) |
| .68 | $CH_2OHCH{:}CHCH_2Cl + H_2O$ | $H_2O$ | 0.1 | - | - | $k$A | 30 | 2.0 | -5 | | | | | ([17]) |
| | | | | | | | 50 | 3.67 | -4 | | | | | " |
| .69 | $CH_2OHCH{:}CHCH_2Cl + OH^-$ | $H_2O$ | | | | $k$AB | 30 | 1.48 | -2 | | | | | ([17]) |
| .69.1 | $ClCH{:}CHCH_2Cl + H_2O$ | $H_2O$ | See Supplementary table | | | | | | | | | | | ([11b]) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Mono-aryl-substituted alkyl halide** | | | | | | | | | | | | | |
| .70 | $C_6H_5CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 1.81 | -7 | | | | * | (19) |
| | | | | | 0.03 | | " | 9.25 | -7 | | | | | " |
| | | | | | 0.3 | | " | 1.46 | -5 | | | | | " |
| .71 | $C_6H_5CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | | $k$AB | 81 | 4.15 | -5 | | | | | (19) |
| .72 | $C_6H_5CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | | $k$AB | 76 | 2.64 | -5 | | | | | (19) |
| .73 | $C_6H_5CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $k$A | 30 | 3.7 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 7.7 | -6 | 20.6 | 2.1 | 8 | | |
| | | | | KOH | 0.05 | $k$A | 30 | 2.8 | -6 | | | | | (22b) |
| | | | | | " | | 60 | 4.3 | -5 | | | | | |
| | | | | | 0.10 | | 30 | 5.2 | -6 | | | | | |
| | | | | | " | | 60 | 8.3 | -5 | | | | | |
| | | | | | 0.26 | | 30 | 1.0 | -5 | | | | | |
| | | | | | " | | 60 | 1.7 | -4 | | | | | |
| | | Et50 | ~ 0.01 | | | $k$A | 30 | 1.85 | -6 | | | | | (22a) |
| | | | | | | | 83 | 2.6 | -4 | | | | | |
| | | | See Comments | | | | | | | | | | | (11a) |
| .73.1 | $C_6H_5CH_2Cl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k$A | 25 | 4.17 | -10 | | | | * | (21b) |
| .74 | $dl$-$C_6H_5CH(CH_3)Cl + H_2O$ | $(Me)_2CO$ | A = 0.2 | $HCl + HgCl_2$ | 0.05 | $k$AB | | | | | | | | (24) |
| | | | B = 2.77 | | 0.0 | | 50 | 5.43 | -6 | | | | | " |
| | | | | | 0.1 | | " | 3.89 | -5 | | | | | " |
| | | | | | 0.2 | | " | 2.17 | -4 | | | | | " |
| | | | | | 0.3 | | " | 2.65 | -4 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .74 | *dl*-$C_6H_5CH(CH_3)Cl + H_2O$ *(continued)* | | 5.55 | | 0.0 | | 50 | 2.16 | -7 | | | | | (24) |
| | | | | | 0.1 | | " | 1.05 | -5 | | | | | " |
| | | | | | 0.3 | | " | 1.87 | -4 | | | | | " |
| .75 | *dl*-$C_6H_5CH(CH_3)Br + H_2O$ | $(Me)_2CO$ | A = 0.2 | $HCl + HgBr_2$ | 0.05 | *k* AB | | | | | | | | (24) |
| | | | B = 2.77 | | 0.0 | | 50 | 1.92 | -6 | | | | | " |
| | | | | | 0.05 | | " | 9.74 | -5 | | | | | " |
| | | | | | 0.1 | | " | 2.57 | -4 | | | | | " |
| | | | 5.55 | | 0.0 | " | " | 4.39 | -6 | | | | | " |
| | | | | | 0.05 | | " | 8.66 | -5 | | | | | " |
| .76 | *m*-$CH_3C_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | *k* A | 81 | 5.18 | -7 | | | | * | (19) |
| | | | | | 0.03 | | " | 2.56 | -6 | | | | | " |
| | | | | | 0.3 | | " | 3.34 | -5 | | | | | " |
| .77 | *m*-$CH_3C_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | | *k* AB | 76 | 2.50 | -5 | | | | | (19) |
| .78 | *p*-$CH_3C_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | *k* A | 81 | 1.55 | -7 | | | | * | (19) |
| | | | | | 0.03 | | " | 1.91 | -6 | | | | | " |
| | | | | | 0.3 | | " | 1.93 | -5 | | | | | " |
| .79 | *p*-$CH_3C_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | | *k* AB | 81 | 6.00 | -5 | | | | * | (19) |
| .80 | *p*-$CH_3C_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | | *k* AB | 76 | 3.33 | -6 | | | | | (19) |
| .81 | *o*-$CH_3C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | *k* A | 30 | 1.6 | -6 | | | | * | (22b) |
| | | | | | | | 60 | 3.2 | -5 | 20.2 | 4.7 | 8 | | |
| | | " | " | KOH | 0.05 | *k* A | 30 | 7.0 | -6 | | | | * | " |
| | | | | | 0.10 | | " | 9.7 | -6 | | | | | |
| | | | | | 0.26 | | " | 2.1 | -5 | | | | | |
| | | Et50 | ~ 0.01 | | | *k* A | 30 | 9.2 | -6 | | | | | (22a) |
| | | | | | | | 83 | 1.25 | -3 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .82 | $m\text{-}CH_3C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $k$A | 30 | 4.6 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 9.2 | -6 | 20.4 | 1.8 | 8 | | |
| | | " | " | KOH | 0.05 | $k$A | 30 | 2.7 | -6 | | | | * | " |
| | | | | | 0.10 | | " | 4.7 | -6 | | | | | |
| | | | | | 0.26 | | " | 8.8 | -6 | | | | | |
| | | Et50 | ~ 0.01 | | | $k$A | 30 | 2.4 | -6 | | | | | (22a) |
| | | | | | | | 83 | 3.6 | -4 | | | | | |
| .83 | $p\text{-}CH_3C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $k$A | 30 | 2.9 | -6 | | | | * | (22b) |
| | | | | | | | 60 | 6.7 | -5 | 21.4 | 6.4 | 9 | | |
| | | " | " | KOH | 0.05 | $k$A | 30 | 6.2 | -6 | | | | * | " |
| | | | | | 0.10 | | " | 9.7 | -6 | | | | | |
| | | | | | 0.26 | | " | 1.6 | -5 | | | | | |
| | | Et50 | ~ 0.01 | | | $k$A | 30 | 1.7 | -5 | | | | | (22a) |
| | | | | | | | 83 | 2.7 | -3 | | | | | |
| .84 | $m\text{-}COOHC_6H_4CH_2Cl + H_2O$ | Et50 | ~ 0.01 | | | $k$A | 30 | 3.15 | -7 | | | | | (22a) |
| | | | | | | | 83 | 6.3 | -5 | | | | | |
| | | An50 | ~ 0.01 | | | $k$A | 30 | 9.2 | -8 | | | | * | (22b) |
| | | | | | | | 60 | 2.2 | -6 | 21.7 | 3.1 | 8 | | |
| | | " | " | KOH | 0.05 | $k$A | 30 | 2.75 | -6 | | | | | " |
| | | | | | 0.10 | | " | 6.0 | -6 | | | | | |
| | | | | | 0.26 | | " | 1.6 | -5 | | | | | |
| | $m\text{-}COOHC_6H_4CH_2Cl + OH^-$ | " | A ~ 0.01; B = 0.05 - 0.26 | | | $k$AB | 30 | 6.55 | -5 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .85 | $p$-$COOHC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 6.5 | -8 | | | | * | (22b) |
| | | | | | | | 60 | 1.4 | -6 | 21.1 | 8.2 | 7 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 2.0 | -7 | | | | | " |
| | | | | | | | 83 | 4.3 | -5 | | | | | |
| .86 | $m$-$(CONH_2)C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 50 | 1.3 | -6 | | | | | (22b) |
| | | | | | | | 60 | 3.4 | -6 | 20.9 | 1.4 | 8 | | |
| .87 | $p$-$(CONH_2)C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 50 | 9.2 | -7 | | | | | (22b) |
| | | | | | | | 60 | 2.4 | -6 | 21.0 | 1.2 | 8 | | |
| .88 | $o$-$CNC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 50 | 3.0 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 8.2 | -7 | 21.4 | 7.7 | 7 | | |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 4.0 | -6 | | | | | " |
| | | | | | 0.10 | | " | 7.7 | -6 | | | | | |
| | | | | | 0.26 | | " | 1.7 | -5 | | | | | |
| .89 | $m$-$CNC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 50 | 3.95 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 1.03 | -6 | 20.7 | 3.2 | 7 | | |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 2.8 | -6 | | | | | " |
| | | | | | 0.10 | | " | 5.5 | -6 | | | | | |
| | | | | | 0.26 | | " | 1.5 | -5 | | | | | |
| .90 | $p$-$CNC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.10 | | | $kA$ | 50 | 3.6 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 9.7 | -7 | 21.5 | 9.3 | 7 | | |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 3.7 | -6 | | | | | " |
| | | | | | 0.10 | | " | 7.2 | -6 | | | | | |
| | | | | | 0.26 | | " | 1.5 | -5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .91 | $m$-$NO_2C_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $kA$ | 81 | 3.42 | -8 | | | | * | (19) |
| | | | | | 0.03 | | " | 3.42 | -8 | | | | | " |
| | | | | | 0.3 | | " | 8.20 | -7 | | | | | " |
| .92 | $m$-$NO_2C_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | - | - | $kAB$ | 81 | 9.30 | -5 | | | | * | (19) |
| .93 | $m$-$NO_2C_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | - | $kAB$ | 76 | 8.95 | -5 | | | | * | (19) |
| .94 | $p$-$NO_2C_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $kA$ | 81 | 2.67 | -8 | | | | * | (19) |
| | | | | | 0.03 | | " | 2.70 | -8 | | | | | " |
| | | | | | 0.3 | | " | 8.70 | -7 | | | | | " |
| .95 | $o$-$NO_2C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 2.7 | -8 | | | | | (22b) |
| | | | | | | | 60 | 7.5 | -7 | 22.7 | 4.7 | 8 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 8.7 | -8 | | | | | (22a) |
| | | | | | | | 83 | 2.2 | -5 | | | | | |
| .96 | $m$-$NO_2C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 3.6 | -8 | | | | | |
| | | | | | | | 60 | 8.5 | -7 | 21.7 | 1.2 | 8 | | (22b) |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 1.05 | -7 | | | | | (22a) |
| | | | | | | | 83 | 2.3 | -5 | | | | | |
| .97 | $p$-$NO_2C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 3.3 | -8 | | | | | (22b) |
| | | | | | | | 60 | 7.7 | -7 | 21.5 | 8.2 | 7 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 8.2 | -8 | | | | | (22a) |
| | | | | | | | 83 | 1.9 | -5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .98 | $m$-$FC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 6.29 | -8 | | | | * | ([19]) |
| | | | | | 0.03 | | " | 1.08 | -7 | | | | | " |
| | | | | | 0.3 | | " | 1.22 | -6 | | | | | " |
| .99 | $m$-$FC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | - | $k$AB | 81 | 3.35 | -5 | | | | * | ([19]) |
| .100 | $m$-$FC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | - | $k$AB | 76 | 2.69 | -5 | | | | * | ([19]) |
| .101 | $p$-$FC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 2.41 | -7 | | | | * | ([19]) |
| | | | | | 0.03 | | " | 1.60 | -6 | | | | | " |
| | | | | | 0.3 | | " | 2.55 | -5 | | | | | " |
| .102 | $p$-$FC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | - | $k$AB | 81 | 6.00 | -5 | | | | * | ([19]) |
| .103 | $p$-$FC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | - | $k$AB | 76 | 3.61 | -5 | | | | | ([19]) |
| .104 | $o$-$ClC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 1.04 | -7 | | | | * | ([19]) |
| | | | | | 0.03 | | " | 3.25 | -7 | | | | | " |
| | | | | | 0.3 | | " | 2.65 | -6 | | | | | " |
| .105 | $o$-$ClC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | - | $k$AB | 81 | 4.48 | -5 | | | | * | ([19]) |
| .106 | $m$-$ClC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 5.76 | -8 | | | | * | ([19]) |
| | | | | | 0.03 | | " | 1.01 | -7 | | | | | " |
| | | | | | 0.3 | | " | 1.09 | -6 | | | | | " |
| .107 | $m$-$ClC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | - | $k$AB | 81 | 3.38 | -5 | | | | * | ([19]) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .108 | $p$-$ClC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $kA$ | 81 | 1.44 | -7 | | | | * | (19) |
| | | | | | 0.03 | | " | 5.43 | -7 | | | | | " |
| | | | | | 0.3 | | " | 6.22 | -6 | | | | | " |
| .109 | $p$-$ClC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | - | - | $kAB$ | 81 | 7.10 | -5 | | | | * | (19) |
| .110 | $o$-$ClC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 1.02 | -7 | | | | | (22b) |
| | | | | | | | 60 | 2.3 | -6 | 21.2 | 1.6 | 8 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 83 | 9.2 | -5 | | | | | (22a) |
| .111 | $m$-$ClC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 6.7 | -8 | | | | | (22b) |
| | | | | | | | 60 | 1.55 | -6 | 21.5 | 1.6 | 8 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 2.5 | -7 | | | | | (22a) |
| | | | | | | | 83 | 6.1 | -5 | | | | | |
| .112 | $p$-$ClC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 2.1 | -7 | | | | | (22b) |
| | | | | | | | 60 | 4.5 | -6 | 20.9 | 1.8 | 8 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 8.7 | -7 | | | | | (22a) |
| | | | | | | | 83 | 1.6 | -4 | | | | | |
| .113 | $o,p$-$Cl_2C_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 60 | 1.7 | -8 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $kA$ | 60 | >3 | -8 | | | | | " |
| | | | | | 0.10 | | " | >3.5 | -8 | | | | | |
| | | | | | 0.26 | | " | >5.5 | -8 | | | | | |
| .114 | $o$-$BrC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $kA$ | 81 | 5.22 | -8 | | | | * | (19) |
| | | | | | 0.03 | | " | 1.28 | -7 | | | | | " |
| | | | | | 0.3 | | " | 1.60 | -6 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .115 | $o$-$BrC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | – | $k$AB | 81 | 2.50 | −5 | | | | * | (19) |
| .116 | $o$-$BrC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | – | $k$AB | 76 | 1.53 | −5 | | | | | (19) |
| .117 | $m$-$BrC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 6.34 | −8 | | | | * | (19) |
| | | | | | 0.03 | | " | 9.06 | −8 | | | | | " |
| | | | | | 0.3 | | " | 1.04 | −6 | | | | | " |
| .118 | $m$-$BrC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | – | $k$AB | 81 | 3.62 | −5 | | | | * | (19) |
| .119 | $m$-$BrC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | – | $k$AB | 76 | 3.33 | −5 | | | | | (19) |
| .120 | $p$-$BrC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $k$A | 81 | 1.35 | −7 | | | | * | (19) |
| | | | | | 0.03 | | " | 4.80 | −7 | | | | | " |
| | | | | | 0.3 | | " | 5.06 | −6 | | | | | " |
| .121 | $p$-$BrC_6H_4CH_2F + OH^-$ | Et64 | A = 0.07; B = 0.3 | | – | $k$AB | 81 | 6.25 | −5 | | | | * | (19) |
| .122 | $p$-$BrC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | – | $k$AB | 76 | 3.97 | −5 | | | | | (19) |
| .123 | $o$-$BrC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $k$A | 30 | 9.2 | −8 | | | | * | (22b) |
| | | | | | | | 60 | 2.15 | −6 | 21.5 | 2.4 | 8 | | |
| | | " | " | KOH | 0.05 | $k$A | 30 | 1.8 | −6 | | | | * | (22b) |
| | | | | | 0.10 | | " | 3.7 | −6 | | | | | |
| | | | | | 0.26 | | " | 7.8 | −6 | | | | | |
| | | Et50 | ~ 0.01 | | | $k$A | 30 | 3.9 | −7 | | | | | (22a) |
| | | | | | | | 83 | 7.4 | −5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .124 | $m$-$BrC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 6.5 | -8 | | | | * | (22b) |
| | | | | | | | 60 | 1.55 | -6 | 21.7 | 2.05 | 8 | | |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 1.5 | -6 | | | | | " |
| | | | | | 0.10 | | " | 2.8 | -6 | | | | | |
| | | | | | 0.26 | | " | 6.2 | -6 | | | | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 2.45 | -7 | | | | | (22a) |
| | | | | | | | 83 | 5.6 | -5 | | | | | |
| .125 | $p$-$BrC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 1.8 | -7 | | | | * | (22b) |
| | | | | | | | 60 | 3.9 | -6 | 20.9 | 1.6 | 8 | | |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 2.85 | -6 | | | | * | " |
| | | | | | 0.10 | | " | 5.7 | -6 | | | | | |
| | | | | | 0.26 | | " | 1.67 | -5 | | | | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 7.6 | -7 | | | | | (22a) |
| | | | | | | | 83 | 1.3 | -4 | | | | | |
| .126 | $o,o$-$Br_2C_6H_3CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 4.2 | -8 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 2.4 | -6 | | | | * | (22b) |
| | | | | | 0.10 | | " | 4.3 | -6 | | | | | |
| | | | | | 0.26 | | " | 7.5 | -6 | | | | | |
| .127 | $m,m$-$Br_2C_6H_3CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 2.2 | -8 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 1.5 | -6 | | | | * | (22b) |
| | | | | | 0.10 | | " | 2.8 | -6 | | | | | |
| | | | | | 0.26 | | " | 6.0 | -6 | | | | | |

212.471.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .128 | $o,p\text{-}Br_2C_6H_3CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 7.0 | -8 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $kA$ | 30 | 3.0 | -6 | | | | * | (22b) |
| | | | | | 0.10 | | " | 5.8 | -6 | | | | | |
| | | | | | 0.28 | | " | 1.2 | -5 | | | | | |
| .129 | $m\text{-}IC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $kA$ | 81 | 6.34 | -6 | | | | * | (19) |
| | | | | | 0.03 | | " | 9.06 | -6 | | | | | " |
| | | | | | 0.3 | | " | 1.02 | -6 | | | | | " |
| .130 | $m\text{-}IC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | - | $kAB$ | 76 | 3.58 | -5 | | | | | (19) |
| .131 | $p\text{-}IC_6H_4CH_2F + C_2H_5OH$ | Et64 | 0.07 | HCl | 0 | $kA$ | 81 | 1.12 | -7 | | | | * | (19) |
| | | | | | 0.03 | | " | 4.6 | -7 | | | | | " |
| | | | | | 0.3 | | " | 4.8 | -8 | | | | | " |
| .132 | $p\text{-}IC_6H_4CH_2F + OH^-$ | Et64 | A = B = 0.22 | | - | $kAB$ | 81 | 7.16 | -5 | | | | * | (19) |
| .133 | $p\text{-}IC_6H_4CH_2F + OC_2H_5^-$ | Et95 | A = B = 0.22 | | - | $kAB$ | 76 | 4.45 | -5 | | | | | (19) |
| .134 | $o\text{-}IC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 9.7 | -8 | | | | | (22b) |
| | | | | | | | 60 | 2.1 | -6 | 20.9 | 8.2 | 7 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 4.1 | -7 | | | | | (22a) |
| | | | | | | | 83 | 7.4 | -5 | | | | | |
| .135 | $m\text{-}IC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $kA$ | 30 | 6.6 | -8 | | | | | (22b) |
| | | | | | | | 60 | 1.5 | -6 | 21.2 | 1.1 | 8 | | |
| | | Et50 | ~ 0.01 | | | $kA$ | 30 | 2.5 | -7 | | | | | (22a) |
| | | | | | | | 83 | 5.2 | -5 | | | | | |



942151 O—51——13

212.471.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .136 | $p$-$IC_6H_4CH_2Cl + H_2O$ | An50 | ~ 0.01 | | | $k$A | 30 | 1.7 | -7 | | | | | ([22b]) |
| | | | | | | | 60 | 3.6 | -6 | 20.9 | 1.6 | 8 | | |
| | | Et50 | ~ 0.01 | | | $k$A | 30 | 6.95 | -7 | | | | | ([22a]) |
| | | | | | | | 83 | 1.2 | -4 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Aryloxy-substituted primary alkyl halide** | | | | | | | | | | | | | |
| .137 | $C_6H_5O(CH_2)_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 97 | 2.61 | −7 | | | | | (4) |
| .138 | $o$-$CH_3C_6H_4O(CH_2)_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 97 | 3.29 | −6 | | | | | (4) |
| .139 | $m$-$CH_3C_6H_4O(CH_2)_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 97 | 2.72 | −6 | | | | | (4) |
| .140 | $p$-$CH_3C_6H_4O(CH_3)_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 97 | 3.55 | −6 | | | | | (4) |
| .141 | $p$-$ClC_6H_4O(CH_2)_2Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 97 | 1.55 | −6 | | | | | (4) |
| .142 | $C_6H_5O(CH_2)_3Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 86 | 2.35 | −6 | | | | | (4) |
| | | | | | | | 97 | 8.32 | −6 | 24.3 | | | | " |
| .143 | $C_6H_5O(CH_2)_4Br + H_2O$ | PhOH | B = 0.5; L = 0.1; M = 0.05 | | | $k$ AB | 86 | 8.82 | −6 | 25.8 | | | | (4) |
| | **Arylthio substituted primary alkyl halide** | | | | | | | | | | | | | |
| .144 | $p$-$CH_3C_6H_4S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 25 | 1.70 | −3 | | | | * | (1) |
| | | | | | | | 55 | 3.05 | −2 | 18.8 | | | | " |
| .145 | s-$(CH_3)_3C_6H_2S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 25 | 3.23 | −3 | | | | * | (1) |
| | | | | | | | 55 | 6.53 | −2 | 19.6 | | | | " |
| .146 | $p$-$CH_3OC_6H_4S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 4.34 | −2 | | | | * | (1) |
| .147 | $p$-$NO_2C_6H_4S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 7.5 | −4 | | | | * | (1) |
| | | | | | | | 75 | 4.17 | −3 | 19.8 | | | | " |
| .148 | $p$-$ClC_6H_4S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 1.02 | −2 | | | | * | (1) |
| | | | | | | | 75 | 4.35 | −2 | 16.2 | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .149 | $p$-$BrC_6H_4S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 8.45 | -3 | | | | * | (1) |
| | | | | | | | 75 | 3.32 | -2 | 15.6 | | | | " |
| .150 | $p$-$IC_6H_4S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 7.10 | -3 | | | | * | (1) |
| | | | | | | | 75 | 3.57 | -2 | 18.4 | | | | " |
| .151 | 2, 5-$Cl_2C_6H_3S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 1.05 | -3 | | | | * | (1) |
| | | | | | | | 75 | 4.62 | -3 | 16.9 | | | | " |
| .152 | s-$Cl_3C_6H_2S(CH_2)_2Cl + H_2O$ | An50 | 0.005 | | | $k$ A | 55 | 5.33 | -4 | | | | * | (1) |
| | | | | | | | 75 | 3.30 | -3 | 20.8 | | | | " |
| | **Di-aryl-substituted alkyl halide** | | | | | | | | | | | | | |
| .153 | $(C_6H_5)_2CHCl + H_2O$ | $(Me)_2CO$ | A ~ 0.1 | | | $k$ AB | | | | | | | | (30) |
| | | | B = | 0.5556 | | | 50 | 6.39 | -7 | | | | | " |
| | | | | 1.1112 | | | " | 1.15 | -6 | | | | | " |
| | | | | 2.7778 | | | " | 4.75 | -6 | | | | | " |
| | | | | 5.5556 | | | " | 1.77 | -5 | | | | | " |
| .154 | $(C_6H_5)_2CHCl$ + $C_2H_5OH$ (a) | EtOH + $H_2O$ % | 0.03 - 0.14 | | | | | | | | | | * | (22) |
| | $H_2O$ (b) | 0 | | | (a + b) | = $k$ A | 0 | 1.80 | -6 | | | | | " |
| | | 0 | | | | " | 25 | 4.84 | -5 | 21.3 | | | | |
| | | 0 | | | (a + b) | = $k$ AB | 25 | 4.85 | -5 | | | | * | " |
| | | 0.15 | | | | | " | 5.28 | -5 | | | | | " |
| | | 0.58 | | | | | " | 5.98 | -5 | | | | | " |
| | | 1.07 | | | | | " | 6.80 | -5 | | | | | " |
| | | 2.39 | | | | | " | 8.86 | -5 | | | | | " |
| | | 7.19 | | | | | " | 1.92 | -4 | | | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .155 | $(C_6H_5)_2CHCl + C_2H_5OH$ | B | 0.4 – 0.1 | | | $k$ A | 25 | 5.76 | –5 | | | | * | (9) |
| | | | 0.6 – 0.1 | $H_2O$ | 0.86 | " | " | 6.70 | –5 | | | | | " |
| | | | | " | 1.58 | " | " | 1.15 | –4 | | | | | " |
| | | | 0.1 | $PhNO_2$ | 0.3 – 0.6 | " | " | 4.38 | –5 | | | | | " |
| | | | 0.09 | HCl | 0.2 – 0.4 | " | " | 6.80 | –5 | | | | | " |
| .156 | $(C_6H_5)_2CHCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k$ A | 25 | 8.41 | –7 | | | | * | (21b) |
| | | | | | | | 30 | 2.0 | –6 | 26.6 | 5.0 | 11 | | |
| .157 | $(p\text{-}CH_3OC_6H_4)_2CHCl + CH_3OH$ | $PhNO_2$ | A ~ 0.07; | $Et_3N$ | ~ 0.1 | $k$ AB + $k'$ $AB^2$ | | | | | | | | (2c) |
| | | B = 0.07 – 0.2 | | | | $k$ | 25 | 2.22 | –3 | | | | | |
| | | | | | | $k'$ | " | 1.0 | –2 | | | | | |
| | **Tri - aryl - substituted alkyl halide** | | | | | | | | | | | | | |
| .158 | $(C_6H_5)_3CCl + H_2O$ | Diox | A = 0.1 – 0.2; | B = 0.1 – 0.5 | | $k$ AB | 50 | 3.3 | –4 | | | | | (23a) |
| .159 | $(C_6H_5)_3CCl + CH_3OH$ | $C_6H_6$ | A = 0.1 | $C_5H_5N$ | 0.1 | $k$ $AB^2$ | 25 | 4.33 | –3 | 6.6 | (25 – 60°) | | * | (27) |
| | | B = 0.03 – 0.19 | | | | | | | | | | | | |
| .160 | $(C_6H_5)_3CCl + C_6H_5OH$ | " | " | " | " | $k$ $AB^2$ | 25 | 6.7 | –5 | | | | * | (27) |
| .161 | $(C_6H_5)_3CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k$ A | 0 | 1.57 | –3 | | | | * | (21b) |
| | | | | | | | 25 | 1.24 | –2 | 13.4 | 1.45 | 6 | | |
| .162 | $(C_6H_5)_3CBr + H_2O$ | $C_6H_6$ | A = 0.1 | $C_5H_5N$ | 0.1 | | 25 | very fast | | | | | * | (27) |
| | | B = 0.03 – 0.19 | | | | | | | | | | | | |
| .163 | $(C_6H_5)_3CBr + CH_3OH$ | " | " | " | " | $k$ $AB^2$ | 25 | ~ 3.7 | –1 | | | | * | (27) |
| .164 | $(C_6H_5)_3CBr + (C_6H_5)_3COH$ | " | " | " | " | $k$ $AB^2$ | 60 | 2.3 | –5 | | | | * | (27) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .165 | $(p\text{-}CH_3C_6H_4)(C_6H_5)_2CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 7.18 | -3 | | | | * | (21b) |
| | | | | | | | 25 | 1.60 | -2 | 12.4 | 1.1 | 6 | | |
| .166 | $(p\text{-}CH_3OC_6H_4)_3CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | > 1.5 | -1 | 26.6 | 5.0 | 11 | * | (21b) |
| .167 | $(p\text{-}(CH_3)_3C.C_6H_4)_3CCl + CH_3OH$ | $C_6H_6$ | A = 0.1 | $C_5H_5N$ | 0.1 | $k\,AB^2$ | 25 | 1.3 | -1 | | | | * | (27) |
| | | B = 0.03 - 0.19 | | | | | | | | | | | | |
| .168 | $(1\text{-}C_{10}H_7)(C_6H_5)_2CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 2.14 | -3 | | | | * | (21b) |
| | | | | | | | 25 | 1.59 | -2 | | 9.2 | 5 | | |
| .169 | $(2\text{-}C_{10}H_7)(C_6H_5)_2CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 2.63 | -3 | | | | * | (21b) |
| | | | | | | | 25 | 1.97 | -2 | 13.0 | 1.15 | 6 | | |
| .170 | $(p\text{-}NO_2C_6H_4)_3CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 1.02 | -5 | | | | * | (21b) |
| | | | | | | | 25 | 1.36 | -4 | 16.7 | 4.0 | 6 | | |
| .171 | $(p\text{-}FC_6H_4)_3CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 1.15 | -3 | | | | * | (21b) |
| | | | | | | | 25 | 9.34 | -3 | 13.6 | 1.4 | 6 | | |
| .172 | $(p\text{-}ClC_6H_4)_3CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 4.96 | -4 | | | | * | (21b) |
| | | | | | | | 25 | 3.97 | -3 | 13.5 | 2.8 | 5 | | |
| .173 | $(p\text{-}BrC_6H_4)_3CCl + C_2H_5OH$ | EtE | ~ 0.001 | | | $k\,A$ | 0 | 5.44 | -4 | | | | * | (21b) |
| | | | | | | | 25 | 3.58 | -3 | 13.2 | 3.3 | 5 | | |
| | **Aryl-substituted halogen-substituted alkyl halide** | | | | | | | | | | | | | |
| .174 | $C_6H_5CHCl_2 + H_2O$ | An50 | ~ 0.01 | | | $k\,A$ | 30 | 3.8 | -6 | | | | * | (22b) |
| | | | | | | | 60 | 1.10 | -4 | | | | | |
| | | " | " | KOH | 0.05 | $k\,A$ | 30 | 3.8 | -6 | | | | * | (22b) |
| | | | | | " | | 60 | 1.12 | -4 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .174 | $C_6H_5CHCl_2 + H_2O$ *(continued)* | An50 | ~ 0.01 | KOH | 0.10 | $k$ A | 30 | 3.7 | −6 | | | | | |
| | | | | | " | | 60 | 1.07 | −4 | | | | | |
| | | | | | 0.26 | | 30 | 3.2 | −6 | | | | | |
| | | | | | " | | 60 | 0.87 | −4 | | | | | |
| .175 | $C_6H_5CCl_3 + H_2O$ | An50 | 0.01 | | | $k$ A | 30 | 1.8 | −4 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $k$ A | 30 | 1.8 | −4 | | | | * | " |
| | | | | | 0.10 | | " | 1.8 | −4 | | | | | |
| | | | | | 0.26 | | " | 1.45 | −4 | | | | | |
| | | " | " | $CH_3COOK$ | 0.25 | " | 30 | 1.43 | −4 | | | | * | " |
| | | " | " | $KNO_3$ | 0.25 | " | 30 | 1.75 | −4 | | | | * | " |
| .176 | $o$-$ClC_6H_4CHCl_2 + H_2O$ | An50 | ~ 0.01 | | | $k$ A | 60 | 2.2 | −6 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $k$ A | 60 | 2.5 | −6 | | | | * | " |
| | | | | | 0.10 | | " | 2.8 | −6 | | | | | |
| | | | | | 0.26 | | " | 3.3 | −6 | | | | | |
| .177 | $m$-$ClC_6H_4CHCl_2 + H_2O$ | An50 | ~ 0.01 | | | $k$ A | 60 | 1.3 | −6 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $k$ A | 60 | 1.8 | −6 | | | | * | (22b) |
| | | | | | 0.10 | | " | 2.3 | −6 | | | | | |
| | | | | | 0.26 | | " | 3.0 | −6 | | | | | |
| .178 | $p$-$ClC_6H_4CHCl_2 + H_2O$ | An50 | ~ 0.01 | | | $k$ A | 60 | 4.5 | −5 | | | | * | (22b) |
| | | " | " | KOH | 0.05 | $k$ A | 60 | 4.5 | −5 | | | | * | " |
| | | | | | 0.10 | | " | 4.2 | −5 | | | | | |
| | | | | | 0.26 | | " | 3.5 | −5 | | | | | |

## SUPPLEMENTARY TABLES

| Fraction of (elimination) reaction (b) [13] | | | | | | |
|---|---|---|---|---|---|---|
| (.18) | $(CH_3)_2CHBr + OH^-$ | | | | | |
| °C | 45 | 50 | 60 | 75 | 80 | 100 |
| Solvent: Et60 | 0.532 | - | 0.557 | 0.575 | - | 0.636 |
| Et80 | - | 0.581 | - | - | 0.612 | 0.665 |

| Composition of products (molefraction, $N$) at 25° C [3] | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| (.24) $(CH_3)_3CCl + \begin{cases} H_2O \\ CH_3OH \end{cases}$ | | | | | | (.25) $(CH_3)_3CCl + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$ | | | | |
| Solvent | | | Product | | | Solvent | | Product | | |
| MeOH % | MeOH ($N$) | $H_2O$ | $(CH_3)_3COH$ | $(CH_3)_3COCH_3$ | $C_4H_8$ | EtOH % | $H_2O$ | $(CH_3)_3COH$ | $(CH_3)_3COC_2H_5$ | $C_4H_8$ |
| 70 | 0.510 | 0.490 | 0.55 | 0.36 | 0.09 | 60 | 0.683 | 0.715 | 0.155 | 0.13 |
| 85 | 0.716 | 0.284 | 0.28 | 0.59 | 0.13 | 80 | 0.447 | 0.56 | 0.27 | 0.17 |
| 92 | 0.836 | 0.164 | 0.14 | 0.68 | 0.18 | 90 | 0.264 | 0.37 | 0.41 | 0.22 |

## SUPPLEMENTARY TABLES *(continued)*



**(.69.1)** $CHCl{:}CHCH_2Cl + H_2O \rightarrow CHCl{:}CHCH_2OH + HCl$

Solvent $H_2O$; Temperature 80° C ; $x$ = % hydrolyzed after 30 minutes

| Catalyst | Isomer | $x$ |
|---|---|---|
| 0.2 % CuCl, 1.5 % HCl | $\alpha$ | 30 |
| | $\beta$ | 73 |
| 1 % NaOH | $\alpha$ | 39 |
| | $\beta$ | 32 |
| 1.5 % HCl | $\alpha$ | 8 |
| | $\beta$ | 4 |

## SOLVENTS

| | |
|---|---|
| Diox | 1,4 - Dioxane |
| DiW | 1,4 - Dioxane: $H_2O$ = 2:1 (vol) |
| Et 50 (60, 64, 80, 95) | $C_2H_5OH$ (vol % as indicated) + $H_2O$ |
| EtE | $C_2H_5OH$ 40 % + $(C_2H_5)_2O$ 60 % [21b] |
| An 50 (80) | $(CH_3)_2CO$ (vol % as indicated) + $H_2O$ |
| AnD 50 | $(CH_3)_2CO$ 50 vol % + $D_2O$ 50 vol % |
| WAn | 1 l $(CH_3)_2CO$ + 400 g $H_2O$ |
| WEt | 1 l $C_2H_5OH$ + 400 g $H_2O$ |

## COMMENTS

**Classification.** The aliphatic halides undergoing solvolysis are grouped under the headings: Saturated alkyl halide; Carboxyl - substituted alkyl halide; Halogen - substituted alkyl halide; Unsaturated alkenyl halide; Mono-aryl-substituted alkyl halide; Aryloxy - substituted alkyl halide; Arylthio - substituted alkyl halide; Di-aryl-substituted alkyl halide; Tri-aryl-substituted alkyl halide; Aryl-substituted halogen-substituted alkyl halide. In each group, the halides are arranged as usual in the order of increasing numbers of C atoms in the alkyl, straight-chain isomers preceding the branched-chain isomers; the order of halides is F, Cl, Br, I.

**Comments by Literature References.** ([1]) Original $k$ assumed to be in minutes. ([4]) From reverse reaction. ([19]) For alkaline hydrolysis, $k$ calculated from fractions of completion of the reaction in 10 hours, assuming second order. For HCl-catalyzed hydrolysis, $k$ was calculated assuming first order, from fractions of completion in, respectively, 120, 120, and 10 hours, with 0, 0.03, and 0.3 M/l HCl ([21b]) The values of $k$ as listed are valid only for the given concentration; the variation of $k$ with the concentration $c$ = ester + ether is $k = k_1 + k_2/(k_3 + c)$, where the second term stems from a second mechanism, contributing the rate-constant term $k_2/k_3$ at $c = 0$. The preexponential factor is formulated $a + b/(k_3 + c)$. ([22a])([22b]) Rates of the nonalkaline hydrolyses are unaffected by $H_2SO_4$ up to 0.5 M/l. The rates of the alkaline hydrolyses are represented by first-order equations and rate constants; consequently, in the tables, KOH is listed as "addend" not as reactant. KOH is said to exert, in addition to the solvolytic mass-action of $OH^-$, a retarding effect on account of the hydrophilic nature of $K^+$. For the alkaline hydrolysis (.73) and analogous reactions, a good second-order $k$ can be given up to about 0.1 M/l KOH, but this second-order $k$ falls off at higher concentrations of KOH. However, the second-order $k$ remains satisfactorily constant in (.88) owing to presence of the COOH group. In reaction (.158), $CH_3COOK$ has the same effect as KOH, whereas $KNO_3$ has none. ([27]) $C_5H_5N$ acts only as acceptor for the hydrogen halide formed; its occasional replacement by $C_6H_5N(C_2H_5)_2$, $C_9H_7N$, or $\alpha$ - $CH_3C_9H_6N$, does not affect $k$ much. In solvolysis by $CH_3OH$ mixed with $C_6H_5OH$ or substituted phenols, the rate law is $k$AB [PhOH] (data of $k$ in original). See further displacement reactions with amines, 332.751.

**Comments by Reactions.** **(.1)** In $H_2O$: Arrhenius equation not applicable; $\log k = 110.223 - (10403/T) - 33.559 \log T$. **(.2)** In $H_2O$ Arrhenius equation not applicable; $\log k = 112.656 - (10236/T) - 34.259 \log T$. **(.3)** In $H_2O$ Arrhenius equation not applicable; $\log k = 111.859 - (10534/T) - 33.821 \log T$. **(.4)** Reaction with KOH in

## COMMENTS *(continued)*

abs. EtOH. **(.6.1)** As (.4); $k$ independent of A, but varying with B. Data of $k$ are averages for B = 0.01 - 0.1. **(.12)** As (.4). **(.17)** The second-order $k$ are derived from the overall reaction (a + b) (.18). **(.24) (.25) (.26)** The kinetics of the simultaneous hydrolysis + alcoholysis have been represented ([23]) by two-term second-order rate equations, in terms of partial vapor pressures of the components, of the type $-d(A/A_o)/dt = k_w AB_w + k_a AB_a$, with the notation A = tert-BuCl, $B_w = H_2O$, $B_a$ = alcohol ($CH_3OH$ or $C_2H_5OH$), subscript $_o$ referring to the pure substance; The constant $k_w$ was derived from the experimental rates of pure hydrolysis in acetone, or in dioxane on the assumption of a second-order law $k_w AB_w$, and, thence, by difference, from the experimental rate of hydrolysis + alcoholysis, on the assumption of the second-order law, the constants $k_a$. However, this formulation fails to render the experimental compositions of the products (see Supplementary Tables). This can be achieved by assuming hypothetical higher-molecular reactions of the type $A + 2B_w$, $A + 2B_a$, and $A + B_w + B_a$, with a three-term and three-constant third-order rate law, or, better, by assuming similar polymolecular reactions of even higher orders, resulting in higher-order rate laws. These laws, and the high-order $k$, obviously purely hypothetical, have not been included in these Tables, and the advantage of expressing mass action in terms of partial pressures has not been deemed convincing. In the judgement of the editor, the experimental data warrant only evaluation in terms of an overall first-order constant for the hydrolysis + alcoholysis. According to ([11]), this constant can be represented by $\log k = 1.232 \log H - 9.811$, where $H$ = Henry's constant of tert-BuCl in the given solvent. **(. 26)** Data for hydrolysis; alcoholysis is disregarded. Under identical conditions, with excess A, $k$ remains constant when, after consumption of the initially present $OH^-$, the solution passes the neutral point into the acid region. **(.32) (.33)** Accompanied by elimination reaction which see 422.471.

**(.34) (.35) (.36)** Reaction (.34) measured directly; similarly, the reactions $CH_3N(CH_2CH_2Cl)_2 + (C_2H_5)_3N \longrightarrow CH_3N(CH_2CH_2Cl)(CH_2CH_2)N(C_2H_5)_3Cl$, with $k = 4.2 \times 10^{-4}$, and $CH_3N(CH_2CH_2Cl)_2 + 2\ Na_2S_2O_3 \longrightarrow CH_3N(CH_2CH_2S_2O_3Na)_2 + 2\ NaCl$, with $k = 3.0 \times 10^{-4}$ (converted to sec from the presumably original hours). The rate-determining step of all these reactions is assumed to be the ionization $CH_3N(CH_2CH_2Cl)_2 \longrightarrow CH_3\overset{+}{N}(CH_2CH_2Cl):(CH_2CH_2) + Cl^-$. This step, and its reverse, is assumed to underlie reactions (.35) and (.36), and the simultaneous dimerizations of the type $2\ RN(CH_2CH_2Cl)_2 \longrightarrow R(CH_2CH_2Cl)\overset{+}{N}:(CH_2CH_2)_2:\overset{+}{N}(CH_2CH_2Cl)R + 2\ Cl^-$ (where R = $CH_3$ or $C_2H_5$). For the hydrolyses (.35) and (.36), and the accompanying dimerizations, ([2b]) and ([2a]) give fractional times, and rate constants of the constituent steps calculated with the aid of a differential analyzer on the basis of the

## COMMENTS *(continued)*

assumed mechanisms. **(.46) (.49)** Elimination reaction (c) is about 10 % of the total. **(.51) (.52)** Second-order constants obtained after deduction of first-order terms determined in acid and neutral solutions. **(.53) (.54)** The hypothetical second-order reaction (.54) is considered to be the rate-determining step (followed by $CH(COO^-)(OH_3^+) \rightarrow CH_2(COO^-)OH + H^+$) of the observed reaction (.53). **(.55) (.56)** As (.53) (.54). **(.59)** Second step of hydrolysis becomes noticeable at 60°C. **(.65)** First-order $k$ falls with time, indicating presence of some second-order reaction; second-order $k$ calculated disregarding the first-order reaction. **(.73)** See comments on Literature reference ([22b]). No reaction occurs between the saturated vapors slightly above 100° C, except in contact with a liquid water surface. At 100° C, the rate of production of HCl, in contact with liquid water, can be calculated from the original data to about $2.2 \times 10^{-8}$ moles /sec/cm$^2$(GSF). **(.77)** First-order $k$ constant over 25 % of the reaction, then falling off. Second-order holding in any direction if difference of forward and back reaction is integrated as a whole. **(.78)** A second-order law in terms of partial pressures, proposed by ([23]), and involving two separate terms, for hydrolysis and alcoholysis, fails to account for the composition of the products ([3]). The catalytic effect of $H_2O$ exceeds greatly its participation as reactant ([9]). **(.84) (.175)** See comments on Literature reference ([22b]).

## LITERATURE

(01) L.J.Andrews, *ACS* 1946, **68**, 2584. (1) G.Baddeley, G.M.Bennett, *CSL* **1933**, 261. (2) P.D.Bartlett, *ACS* 1939, **61**, 1630. (2a) P.D.Bartlett, J.W.Davies, S.D.Ross, C.G.Swain, *ACS* 1947, **69**, 2977. (2b) P.D.Bartlett, S.D.Ross, C.G.Swain, *ACS* 1947, **69**, 2971. (2c) P.D.Bartlett, R.W.Nebell, *ACS* 1940, **82**, 1345. (3) L.C.Bateman, E.D.Hughes, C.K.Ingold, *CSL* **1938**, 881; *ACS* 1938, **60**, 3080. (4) G. M. Bennett, F. M. Reynolds, *CSL* **1935**, 131. (5) H. M. Dawson, N. B. Dyson, *CSL* 1933, **49**, 1133. (6) H. M. Dawson, E. R. Pycock, G. F. Smith, *CSL* **1943**, 517. (7) S.Eagle, J.C.Warner, *CSL* 1939, **61**, 488. (8) R.A.Fairclough, C.N.Hinshelwood, *CSL* **1937**, 538. (9) N.F.Farinacci, L.P.Hammett, *ACS* 1937, **57**, 2542; 1938, **60**, 3097. (10) C. H. Grant, C. N. Hinshelwood, *CSL* **1933**, 258.

(11) Grunwald, S. Winstein, *ACS* 1948, **70**, 846. (11a) G. Harker, *CSL* 1924, **125**, 500. (11b) L. F. Hatch, G. B. Roberts, *ACS* 1946, **68**, 1196. (12) E. D. Hughes, *CSL* **1935**, 255. (13) E.D.Hughes, C. K. Ingold, U. G. Shapiro, *CSL* **1936**, 225. (14) E. D. Hughes, C. K. Ingold, U. G. Shapiro, *CSL* **1937**, 1277. (14a) E.D.Hughes, B.J.McNulty, *CSL* **1937**, 1283. (15) E.D.Hughes, U.G.Shapiro, *CSL* **1937**, 1177. (16) E.D.Hughes, U. G. Shapiro, *CSL* **1937**, 1192. (16a) E. D. Hughes, *TFS* 1941, **37**, 603. (17) R. Kadesch, *ACS* 1946, **68**, 46. (18) C. L. McCabe, J. C. Warner, *ACS* 1948, **70**, 4031. (19) W. T. Miller, jr., J. Bernstein, *ACS* 1948, **70**, 3600. (20) E.A.Moelwyn-Hughes, *CSL* **1933**, 1576.

(21) E.A.Moelwyn-Hughes, *PRS*$^{A}$ 1938, **164**, 295. (21a) E. A. Moelwyn-Hughes, *PRS*$^{A}$ 1949, **196**, 540. (21b) A. C. Nixon, G. E. K. Branch, *ACS* 1936, **58**, 492. (22) J. Norris, A. Morton, *ACS* 1928, **50**, 1795. (22a) S.C.J.Olivier et al., *RTC* 1922, **41**, 301, 646; 1923, **42**, 516. (22b) S.C.J.Olivier et al., *RTC* 1930, **49**, 697, 996; 1934, **54**, 869, 1087; 1937, **56**, 247. (23) A.R.Olsen, R.S.Halford, *ACS* 1937, **59**, 2644. (23a) D.R.Read, W.Taylor, *CSL* **1939**, 478. (24) D. R. Read, W. Taylor, *CSL* **1940**, 679. (25) G. F. Smith, *CSL* **1943**, 521. (26) J. E. Stevens, C. L. McCabe, J. C. Warner, *ACS* 1948, **70**, 2449. (27) C. G. Swain, *ACS* 1948, **70**, 1119. (28) W.Taylor, *CSL* **1937**, 992. (29) W.Taylor, *CSL* **1938**, 841. (30) W. Taylor, *ACS* 1938, **60**, 2094.

(31) E.W.Timm, C.N.Hinshelwood, *CSL* **1938**, 862. (32) S.Winstein, *ACS* 1939, **61**, 1635. (33) W.G.Young, L.J.Andrews, *ACS* 1944, **66**, 421.

# SOLVOLYSIS

## Aryl halides

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $ArX + OR^- \rightarrow ArOR + X^-$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ |
| .1 | $p\text{-}NO_2C_6H_4Br + OCH_3^-$ | $CH_3OH$ | A = B = 0.002 | $k$ AB | 99 | 7.8 | −4 |
| .2 | $p\text{-}(CH_3SO_2)C_6H_4Br + OCH_3^-$ | $CH_3OH$ | A = B = 0.002 | $k$ AB | 99 | 2.8 | −5 |

## LITERATURE

T. F. Bunnet, Arnold Levitt, *ACS* 1948, 70, 2778.

# ESTER SOLVOLYSIS

## Alkyl halide + Phenolate

*Liquid phase*

Reaction type $RX + ArO^- \rightarrow ROAr + X^-$

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 42.5 | 1.23 | -3 | | | (2) |
| | | | 0.250 | | " | 1.50 | -3 | | | |
| | | | 0.1875 | | " | 1.64 | -3 | | | |
| | | | 0.125 | | " | 2.11 | -3 | | | |
| | | | 0.375 | " | 50 | 2.57 | -3 | | | |
| | | | 0.250 | | " | 2.85 | -3 | | | |
| | | | 0.1875 | | " | 3.27 | -3 | | | |
| | | | 0.125 | | " | 4.18 | -3 | | | |
| | | | 0.100 | | " | 5.18 | -3 | | | |
| | | | 0.500 | " | 55 | 3.63 | -3 | | | |
| | | | 0.375 | | " | 3.76 | -3 | | | |
| | | | 0.250 | | " | 4.59 | -3 | | | |
| | | | 0.1875 | | " | 5.02 | -3 | | | |
| | | | 0.125 | | " | 6.16 | -3 | 18.9 | | |
| .2 | $C_2H_5I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 50 | 5.94 | -4 | | * | (2) |
| | | | 0.250 | | " | 7.96 | -4 | | | |
| | | | 0.125 | | " | 1.09 | -3 | | | |



942151 O—51——14

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $C_2H_5I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ *(continued)* | | 0.500 | $k$ AB | 57.7 | 1.17 | -3 | | | (2) |
| | | | 0.250 | | " | 1.46 | -3 | | | |
| | | | 0.125 | | " | 2.07 | -3 | | | |
| | | | 0.250 | " | 68 | 3.49 | -3 | | | " |
| | | | 0.125 | | " | 4.98 | -3 | 19.0 | | |
| .3 | $C_2H_5I + C_6H_5O^-$ | $CH_3OH$ | 0.1 | $k$ AB | 58.5 | 4.61 | -4 | | * | (1) |
| | | $C_2H_5OH$ | " | | " | 1.04 | -3 | | | |
| | | $C_3H_7OH$ | " | | " | 6.36 | -4 | | | |
| | | *iso* - $C_4H_9OH$ | " | | " | 3.12 | -4 | | | |
| | | *iso* - $C_5H_{11}OH$ | " | | " | 2.08 | -4 | | | |
| .4 | $C_3H_7I + C_6H_5O^-$ | $CH_3OH$ | 0.1 | $k$ AB | 58.5 | 1.92 | -4 | | * | (1) |
| | | $C_2H_5OH$ | " | | " | 4.15 | -4 | | | |
| | | $C_3H_7OH$ | " | | " | 2.69 | -4 | | | |
| | | *iso* - $C_4H_9OH$ | " | | " | 1.33 | -4 | | | |
| | | *iso* - $C_5H_{11}OH$ | " | | " | 9.00 | -5 | | | |
| | | $(CH_3)_2CO$ | 0.05 | | " | 1.09 | -3 | | | |
| .5 | $C_3H_7I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 57.5 | 4.24 | -4 | | * | (2) |
| | | | 0.250 | | " | 5.28 | -4 | | | |
| | | | 0.500 | " | 68 | 1.12 | -3 | | | " |
| | | | 0.250 | | " | 1.40 | -3 | | | |
| | | | 0.125 | | " | 2.08 | -3 | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $C_3H_7I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ *(continued)* | | 0.250 | | 75 | 2.05 | -3 | | | ( 2 ) |
| | | | 0.125 | | " | 3.50 | -3 | | | |
| | | | 0.100 | | " | 4.01 | -3 | 21.0 | | |
| .6 | $(CH_3)_2CHI + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 57.5 | 3.06 | -4 | | * | ( 2 ) |
| | | | 0.250 | | " | 4.08 | -4 | | | |
| | | | 0.500 | | 68 | 8.28 | -4 | | | " |
| | | | 0.250 | | " | 1.05 | -3 | | | |
| | | | 0.125 | | " | 1.56 | -3 | | | |
| | | | 0.500 | | 75 | 1.54 | -3 | | | " |
| | | | 0.250 | | " | 1.92 | -3 | | | |
| | | | 0.100 | | " | 3.15 | -3 | | | |
| .7 | $C_4H_9I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 57.5 | 3.97 | -4 | | * | ( 2 ) |
| | | | 0.250 | | " | 5.00 | -4 | | | |
| | | | 0.500 | | 68 | 9.92 | -4 | | | " |
| | | | 0.250 | | " | 1.23 | -3 | | | |
| | | | 0.100 | | " | 2.18 | -3 | | | |
| | | | 0.500 | | 75 | 1.77 | -3 | | | " |
| | | | 0.250 | | " | 2.25 | -3 | | | |
| | | | 0.100 | | " | 3.57 | -3 | 20.6 | | |
| .8 | $C_2H_5CH(CH_3)I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 57.5 | 1.43 | -4 | | * | ( 2 ) |
| | | | 0.250 | | " | 1.82 | -4 | | | |
| | | | 0.500 | | 68 | 3.72 | -4 | | | " |
| | | | 0.250 | | " | 4.46 | -4 | | | |
| | | | 0.125 | | " | 7.30 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $C_2H_5CH(CH_3)I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | | 0.500 | | 75 | 5.45 | -4 | | | |
| | | | 0.250 | | " | 7.46 | -4 | | | |
| | *(continued)* | | 0.125 | | " | 1.64 | -3 | 19.6 | | |
| .9 | $C_2H_5I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 57.5 | 3.77 | -4 | | * | ([2]) |
| | | | 0.250 | | " | 4.80 | -4 | | | |
| | | | 0.375 | | 68 | 1.01 | -3 | | | " |
| | | | 0.125 | | " | 1.67 | -3 | | | |
| | | | 0.500 | | 75 | 1.69 | -3 | | | " |
| | | | 0.100 | | " | 3.33 | -3 | 20.3 | | |
| .10 | $C_3H_7CH(CH_3)I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ | $C_2H_5OH$ | A = B = 0.500 | $k$ AB | 57.5 | 2.18 | -4 | | * | ([2]) |
| | | | 0.250 | | " | 2.82 | -4 | | | |
| | | | 0.500 | | 68 | 4.85 | -4 | | | " |
| | | | 0.250 | | " | 6.82 | -4 | | | |
| | | | 0.125 | | " | 1.13 | -3 | | | |
| | | | 0.500 | | 75 | 8.32 | -4 | | | " |
| | | | 0.250 | | " | 1.69 | -3 | | | |
| | | | 0.100 | | " | 2.13 | -3 | 19.4 | | |

## COMMENTS

(.1) (.2) Addition of NaI lowers $k$ slightly. Data of ([2]): selected points.

## LITERATURE

([1]) D.Segaller, *CSL* 1914, **105**, 113. ([2]) S.S.Woolf, *CSL* **1937**, 1172.

# SOLVOLYSIS

## Mercaptyl carboxylate

*Liquid phase*

Reaction type $R'COSR + \begin{Bmatrix} H_2O \\ OH^- \end{Bmatrix} \longrightarrow RSH + \begin{Bmatrix} R'COOH \\ R'COO^- \end{Bmatrix}$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COSC_2H_5 + H_2O$ | $H_2O + (CH_3)_2CO$ 24.6 wt % | 0.1 | HCl | 0.1 | $kA[H^+]$ | 30.0 | 8.0 | -6 | | | |
| | | | | | | | 40.0 | 2.05 | -5 | 17.5 | | |
| | | 43.0 | 0.15 | " | 0.24 | " | 30.0 | 3.83 | -6 | | | |
| | | | | | | | 40.0 | 1.08 | -5 | 18.0 | | |
| | | 62.0 | 0.1 | " | 0.1 | " | 30.0 | 2.30 | -6 | | | |
| | | | | | | | 40.0 | 5.82 | -6 | 18.0 | | |
| .2 | $CH_3COSC_2H_5 + OH^-$ | $H_2O + (CH_3)_2CO$ 24.6 wt % | A = 0.03 - 0.06; B = 0.06 - 0.1 | | | $kAB$ | 10.0 | 2.08 | -2 | | | |
| | | | | | | | 20.0 | 4.67 | -2 | 13.0 | 1.6 | 10 |
| | | 43.0 | " | | | " | 10.0 | 1.43 | -2 | | | |
| | | | | | | | 20.0 | 3.26 | -2 | 13.8 | 4.0 | 10 |
| | | 62.0 | " | | | " | 10.0 | 1.07 | -2 | | | |
| | | | | | | | 20.0 | 2.57 | -2 | | | |
| | | | | | | | 30.0 | 5.76 | -2 | 14.4 | 8.0 | 10 |

## LITERATURE

J.R.Schaefgren, *ACS* 1948, **70**, 1308.

# ESTER EXCHANGE

## Aliphatic alcohol + Alkyl carboxylate

Reaction type $R_1OH + R'COOR_2 \rightarrow R_2OH + R'COOR_1$
(A) (B) (L) (M)

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Medium | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $g$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_4H_9OH + CH_3COOC_2H_5$ | pure liquid | A/B = 1 | $H_2SO_4$ | 0.1 % | $k$ AB | 60 | 3.2 | −5 | |
| | | | 1.55 | | " | | " | 3.4 | −5 | |
| | | | 1 | | 0.2 | | " | 6.1 | −5 | |
| | | | 1.55 | | " | | " | 6.1 | −5 | |
| | | | 1 | | 0.1 | " | 70 | 5.2 | −5 | |
| | | | 1.55 | | " | | " | 5.5 | −5 | |
| | | | 1 | | 0.2 | | " | 1.10 | −4 | |
| | | | 1.55 | | " | | " | 1.12 | −4 | |
| | | | 1 | | 0.1 | | 80 | 9.0 | −5 | |
| | | | 1 | | 0.2 | | " | 1.85 | −4 | 12.8 |
| .2 | $C_2H_5OH + CH_3COOC_4H_9$ | pure liquid | A/B = 1 | $H_2SO_4$ | 0.1 % | $k$ AB | 60 | 3.2 | −5 | |
| | | | | | | | 70 | 5.5 | −5 | |
| | | | | | | | 80 | 8.3 | −5 | |

## COMMENTS

The rate constants of the two opposing reactions (.1) and (.2) are derived from the integrated form of the total rate equation $k_1AB - k_2LM$ which, with one of the $k$ expressed by the equilibrium constant $K = 0.96$, and with the amounts of reactants expressed in *mole fractions*, becomes $kt = \ln A_oB_o / (A_oB_o - L)$. In the given range of $H_2SO_4$, $k$ is proportional to $[H_2SO_4]$. The mechanism is conceived as $B + H^+ \rightarrow BH^+$, and $A + BH^+ \rightleftharpoons L + MH^+$.

## LITERATURE

L. Farkas, O. Schächter, B. H. Vromen, *ACS* 1949, **71**, 1991.

# ESTER EXCHANGE

## Phenol carboxylate + Aliphatic alcohol

*Liquid phase*

Reaction type $R'COOAr + ROH \rightarrow R'COOR + ArOH$

(A) (B) (L) (M)

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 6.30 | -3 | |
| .2 | $CH_3COOC_{10}H_7(\beta) + C_2H_5OH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 1.52 | -3 | |
| .3 | $CH_3COOC_{10}H_7(\beta) + C_3H_7OH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 1.46 | -3 | |
| | | | | | | | | 3.90 | -3 | 12.1 |
| .4 | $CH_3COOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 9.0 | -5 | |
| | | | | | | | 40 | 2.52 | -4 | 12.7 |
| .5 | $C_2H_5COOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 3.96 | -3 | |
| .6 | $C_2H_5COOC_{10}H_7(\beta) + C_2H_5OH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 8.45 | -4 | |
| .7 | $C_2H_5COOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 4.4 | -5 | |
| | | | | | | | 40 | 1.3 | -4 | 13.4 |
| .8 | $C_2H_5COOC_{10}H_7(\beta) + (C_2H_5)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 7.6 | -4 | |
| .9 | $C_3H_7COOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $k$A | 25 | 2.32 | -3 | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .10 | $C_3H_7COOC_{10}H_7(\beta) + C_3H_7OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 4.0 | -4 | |
| | | | | | | | 40 | 1.15 | -3 | 13.0 |
| .11 | $C_3H_7COOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 2.26 | -5 | |
| | | | | | | | 40 | 6.34 | -5 | 12.7 |
| .12 | $(CH_3)_2CHCOOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 9.15 | -4 | |
| .13 | $(CH_3)_2CHCOOC_{10}H_7(\beta) + C_2H_5OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 1.43 | -4 | |
| .14 | $(CH_3)_2CHCOOC_{10}H_7(\beta) + C_3H_7OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 1.22 | -4 | |
| .15 | $(CH_3)_2CHCOOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 5.0 | -6 | |
| | | | | | | | 40 | 1.4 | -5 | 12.7 |
| .16 | $C_4H_9COOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 1.93 | -3 | |
| .17 | $C_4H_9COOC_{10}H_7(\beta) + C_3H_7OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 3.9 | -4 | |
| | | | | | | | 40 | 1.07 | -3 | 12.4 |
| .18 | $C_4H_9COOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 2.06 | -5 | |
| | | | | | | | 40 | 5.90 | -5 | 12.9 |
| .19 | $(CH_3)_3CCOOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 4.5 | -5 | |
| .20 | $(CH_3)_3CCOOC_{10}H_7(\beta) + C_3H_7OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 3.5 | -6 | |
| | | | | | | | 40 | 1.2 | -5 | 12.7 |

| No | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .21 | $(CH_3)_3CCOOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25<br>40 | 9.9<br>4.3 | -8<br>-7 | |
| .22 | $(C_2H_5O)COOC_{10}H_7(\beta) + CH_3OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25 | 1.58 | -5 | |
| .23 | $(C_2H_5O)COOC_{10}H_7(\beta) + C_3H_7OH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25<br>40 | 3.1<br>1.05 | -6<br>-5 | |
| .24 | $(C_2H_5O)COOC_{10}H_7(\beta) + (CH_3)_2CHOH$ | B | 0.006 - 4.0 | HCl | 1 | $kA$ | 25<br>40 | 2.35<br>8.0 | -7<br>-7 | |

## LITERATURE

M.Harfenist, R.Baltzly, *ACS* 1947, **69**, 362

# ESTER EXCHANGE

## Alkyl halide + carboxylic acid

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, Comments, Literature, at the end of the table.

Reaction types $RX + \begin{Bmatrix} R'COOH \\ R'COO^- \end{Bmatrix} \rightarrow R'COOR + \begin{Bmatrix} HX \\ X^- \end{Bmatrix}$

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_5I + CH_3CHOHCOO\ Ag$ | Et 60 | A = B ~ 0.014 − 0.015 | | | $k$ AB | 25 | 2.7 | −2 | * | ([2]) |
| | | | | | | | → | 2.1 | −2 | | |
| | | | ~ 0.03 | | | " | | 5.0 | −2 | | |
| | | | | | | | → | 2.0 | | | |
| .2 | $(COO^-)CH_2Br + HCOO^-$ | $H_2O$ | A = 0.05 − 0.5<br>B = 0 − 0.7 | $NaNO_3$ | 1 − (A + B) | $k$ AB | 25 | 5.5 | −7 | * | ([4]) ([1]) |
| .3 | $(COO^-)CH_2Br + CH_3COO^-$ | $H_2O$ | A = 0.05 − 0.5<br>B = 0 − 0.7 | $NaNO_3$ | 1 − (A + B) | $k$ AB | 25 | 8.3 | −7 | * | ([4]) ([1]) |
| .4 | $(COO^-)CH_2Br + CH_2OHCOO^-$ | $H_2O$ | A = 0.05 − 0.5<br>B = 0 − 0.7 | $NaNO_3$ | 1 − (A + B) | $k$ AB | 25 | 5.8 | −7 | * | ([4]) ([1]) |
| .5 | $(COO^-)CH_2Br + CH_2ClCOO^-$ | $H_2O$ | A = 0.05 − 0.5<br>B = 0 − 0.7 | $NaNO_3$ | 1 − (A + B) | $k$ AB | 25 | 2.3 | −7 | * | ([4]) ([1]) |
| .6 | $(COO^-)CH_2Br + CH_2BrCOO^-$ | $H_2O$ | A = 0.05 − 0.5<br>B = 0 − 0.7 | $NaNO_3$ | 1 − (A + B) | $k$ AB | 25 | 3.2 | −7 | * | ([4]) ([1]) |
| .7 | $CH_3CH{:}CHCH_2Cl + CH_3COOH.NH_2C(NH)N(C_6H_5)_2$ | $CH_3COOH$ | A = B ~ 1.0 | | | $k$ AB | 78.6 | 3.06 | −5 | * | ([3]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $CH_3CH{:}CHCH_2Cl + CH_3COOK$ | $CH_3COOH$ | A = 1.0; B = 0.2 − 1.0 | | | $k$ AB | 78.6 | 2.08 | −5 | * | ([3]) |
| .9 | $CH_2{:}CHCH(CH_3)Cl + CH_3COOK$ | $CH_3COOH$ | A = B ~ 1.0 | | | $k$ AB | 78.6 | 9.5 | −6 | | ([3]) |
| | | | | | | | → | 1.0 | −5 | | |
| | | | A = 1.0; B ~ 0.2 | | | " | | 1.44 | −5 | | |
| | | | | | | | → | 1.77 | −5 | | |
| .10 | $CH_2{:}CHCH(CH_3)Cl + CH_3COOH.NH_2C(NH)N(C_6H_5)_2$ | $CH_3COOH$ | A = B ~ 0.1 | | | $k$ AB | 78.6 | 1.02 | −5 | | ([3]) |
| | | | A = 1.0; B ~ 0.2 | | | $k$ A | " | 4.45 | −6 | | " |
| .11 | $d$-$C_6H_5CH(CH_3)Cl + CH_3COOH$ | $CH_3COOH$ | A = 0.075 − 0.160 | $CH_3COOLi$ | 0.2 | $k$ A | 50 | 3.25 | −6 | * | ([5]) |
| | | | | LiCl 0.15 + $CH_3COOLi$ | 0.5 | | " | 4.85 | −6 | | |
| | | | | LiCl 0.5 + $CH_3COOLi$ | 0.15 | | " | 3.56 | −6 | | |
| | | | $H_2O$ 0.141 + LiCl 0.1 + $CH_3COOLi$ | | 0.1 | | " | 5.20 | −6 | | |
| | | | $H_2O$ 2.18 + LiCl 0.1 + $CH_3COOLi$ | | 0.1 | | " | 6.05 | −6 | | |
| | | | $H_2O$ 3.09 + LiCl 0.1 + $CH_3COOLi$ | | 0.1 | | " | 8.60 | −6 | | |
| .12 | $d$-$C_6H_5CH(CH_3)Cl + CH_3COON(C_6H_5)_4$ | $(CH_3)_2CO$ | 0.05 − 0.15 | | | $k$ AB | 50 | 4.7 | −4 | | ([5]) |

## SOLVENTS

Et 60 $C_2H_5OH$ 60 vol % + $H_2O$ 40 vol %

## COMMENTS

(.1) Partial solvolysis of the $CH_3CHOHCOOC_2H_5$ produced. Considerable fall of $k$ with the progress of the reaction; the lower values of $k$ refer to the reaction after about 3000 sec. (.2)-(.6) log $k$ is a linear function of log $K_b$ (base dissociation constant). (.7) (.8) With the progress of the reaction, increasing amount of $CH_2{:}CHCH(CH_3)OCOCH_3$ in the products. With B = 0.2, some upward drift of $k$ at late stages of the reaction. (.9) Upward drift of $k$ (upper figure after 10 hours) indicates some amount of first-order reaction. Products $CH_2{:}CHCH(CH_3)OCOCH_3$ and $CH_3CH{:}CHCH_2OCOCH_3$ in 51:49% ratio. (.11) (.12) Selected points.

## LITERATURE

(1) H. M. Dawson, N. B. Dyson, *CSL* 1933, 49.

(2) F. G. Donnan, H. E. Potts, *CSL* 1910, 1882.

(3) J. D. Roberts, W. G. Young, S. Winstein, *ACS* 1942, 64, 2157.

(4) G. F. Smith, *CSL* 1943, 521.

(5) J. Steigman, L. P. Hammett, *ACS* 1937, 59, 2536.

# ESTER EXCHANGE

## Carboxylic acid ester + Hydrogen halide

*Liquid phase*

Reaction type $RCOOR' + HX \rightarrow RCOOH + R'X$

Amounts are in M/l.

Rates are in M/l per sec.

Rate measured $-dB/dt$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $CH_3COOCH_3 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 1.44 | -8 |
| .2 | $CH_3COOC_2H_5 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 2.50 | -9 |
| .3 | $CH_3COOC_3H_7 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 2.00 | -9 |
| .4 | $CH_3COOCH(CH_3)_2 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 2.45 | -9 |
| .5 | $CH_3COOCH_2CH{:}CH_2 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 5.92 | -8 |
| .6 | $CH_3COOC_4H_9 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 1.33 | -9 |
| .7 | $CH_3COOCH_2CH(CH_3)_2 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 2.22 | -10 |
| .8 | $CH_3COOCH(CH_3)C_2H_5 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 2.25 | -9 |
| .9 | $CH_3COOC(CH_3)_3 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 3.00 | -4 |
| .10 | $CH_3COOCH_2CH_2OOCCH_3 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 3.11 | -7 |
| .11 | $CH_3COOCH_2CH_2CH(CH_3)_2 + HBr$ | $CH_3COOH$ | $A = B \sim 0.06$ | $k\,AB$ | 18 - 21 | 1.11 | -9 |



942151 O—51——15

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .12 | $CH_3COOC(CH_3)_2C_2H_5 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 4.40 | -4 |
| .13 | $CH_3COOCH_2CH_2CH_2OOCCH_3 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 3.97 | -8 |
| .14 | $CH_3COOCH_2CH(CH_3)OOCCH_3 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 2.92 | -7 |
| .15 | $CH_3COOC_6H_{13} + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 1.67 | -8 |
| .16 | $CH_3COO(cyclo\text{-}C_6H_{11}) + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 1.17 | -8 |
| .17 | $CH_3COOCH_2CH(OCOCH_3)CH_2OOCH_3 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 2.09 | -6 |
| .18 | $CH_3COOCH_2C_6H_5 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 3.15 | -7 |
| .19 | $CH_3COOCH_2CH_2C_6H_5 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | 4.72 | -10 |
| .20 | $CH_3COOC_6H_5 + HBr$ | $CH_3COOH$ | A = B ~ 0.06 | $k$AB | 18 - 21 | no reaction | |

## COMMENTS

**(.10) (.13) (.14)** No allocation for partial reaction with the second $CH_3CO$ group.

**(.20)** No allocation for partial reaction with the second and third $CH_3CO$ group.

## LITERATURE

B.W.Tronow, N.C.Ssigbatullin, *BDC*[B] 1929, **62**, 2850.

# CONDENSATION

## Aromatic aldehyde + Ketone

*Liquid phase*

Reaction type $ArCHO + CH_3COR \longrightarrow ArCH{:}CHCOR + H_2O$

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CHO + CH_3COCH_3$ | $H_2O$ + dioxane 70 % | A = 0.025; B = 0.100 | NaOH | 0.036 | $k$AB | 25 | 1.37 | -3 | |
| | | | | | 0.056 | | " | 1.67 | -3 | |
| | | | | | " | | 50 | 4.65 | -3 | 7.8 |
| .2 | $C_6H_5CHO + CH_3COC_2H_5$ | $H_2O$ + dioxane 70 % | B ~ 0.1<br>A = 0.025 - 0.030 | NaOH | 0.051 | $k$AB | 25 | 6.7 | -4 | |
| | | | | | | | 50 | 1.25 | -3 | 4.8 |
| | | 60 | A = 0.025 | | 0.053 | | 50 | 1.29 | -3 | |
| | | 50 | " | | " | | 50 | 1.30 | -3 | |

## LITERATURE

J. D. Gettler, L. P. Hammett, *JACS* 1943, 65, 1825.

# CONDENSATION

## C = N bond formation

Reaction type $R_1R_2CO + H_2NR \longrightarrow R_1R_2C{:}NR + H_2O$

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.
Solvents, Comments, Literature, at the end of the table

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CHO + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 25 | | 6.0 | 0 | | * | (1) |
| .2 | $(CH_3)_2CO + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 6.35 | -2 | | | (3) |
| | | | | | 25.1 | | 8.61 | -2 | 2.0 | | |
| | | CeW; b 1 | | $k$ AB | 25 | | 9.7 | -2 | | * | (5) |
| | | b 2 | | | " | | 3.97 | -1 | | | |
| .3 | $(CH_3)_2CO + NH_2OH.H^+$ | $H_2O$; pH 1.22 | 0.003 | $k$ AB | 17 - 19 | | 2.16 | -2 | | * | (2) |
| | | 2.18 | | | | | 1.89 | -1 | | | |
| | | 3.80 | | | | | 1.23 | 0 | | | |
| | | 4.86 | | | | | 1.50 | 0 | | | |
| | | 6.39 | | | | | 5.85 | -1 | | | |
| | | 7.97 | | | | | 1.06 | -1 | | | |
| .4 | $CH_3COCOOH + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 25 | | 1.23 | -1 | | * | (1) |
| .5 | $C_3H_7CHO + NH_2NHCONH_2$ | CeW; b 1 | | $k$ AB | 25 | | 1.9 | 0 | | * | (5) |
| | | b 2 | | | | | fast | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $(C_2H_5)_2CO + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 6.9 | -3 | | | (3) |
| | | | | | 25.0 | | 8.5 | -3 | 1.4 | | |
| | | CeW; b 1 | | $k$ AB | 25 | | 2.83 | -2 | | * | (5) |
| | | b 2 | | | " | | 1.85 | -1 | | | |
| .7 | $(CH_3)_3CCHO + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 25 | | 3.33 | -1 | | | (1) |
| .8 | $(CH_3)_3CCOCH_3 + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 7.71 | -4 | | | (3) |
| | | | | | 25.0 | | 1.00 | -3 | 1.8 | | |
| | | CeW; b 1 | | $k$ AB | 25 | | 6.8 | -3 | | * | (5) |
| | | b 2 | | | " | | 2.47 | -2 | | | |
| .9 | $\underbrace{CH_2(CH_2)_3CO}$ + $NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 8.2 | -3 | | | (3) |
| | | | | | 25.0 | | 1.5 | -2 | 4.0 | | |
| .10 | $\underbrace{CH_2(CH_2)_4CO}$ + $NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 4.37 | -1 | | | (3) |
| | | | | | 25.1 | | 5.12 | -1 | 1.1 | | |
| | | CeW; b 1 | | $k$ AB | 25 | | 4.15 | -1 | | * | (5) |
| | | b 2 | | | " | | fast | | | | |
| .11 | $C_6H_{13}CHO + NH_2NHCONH_2$ | CeW; b 1 | | $k$ AB | 25 | | 1.13 | 0 | | * | (5) |
| | | b 2 | | | | | fast | | | | |
| .12 | $C_9H_{17}CHO + NH_2NHCONH_2$ | CeW; b 1 | | $k$ AB | 25 | | 5.3 | -1 | | * | (5) |
| | citronellal | b 2 | | " | " | | fast | | | | |
| .13 | $d\text{-}CH_3C\langle^{CHCH_2}_{COCH_2}\rangle CHC\langle^{CH_2}_{CH_3}$ + $NH_2NHCONH_2$ | Et 83 | A = B = B.HCl = 0.015 | $k$ A | 30 | | 6.24 | -5 | | * | (1a) |
| | | | | | 40 | | 1.28 | -4 | | | |
| | (carvone) | | | | 50 | | 2.67 | -4 | | | |
| | | | See Supplementary table | | | | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .14 | d-$CH_3C$<(CHCH$_2$ / COCH$_2$)>CHC<($CH_2$ / $CH_3$) + $NH_2NHCONH_2$ (carvone) | Et 83 | A = 0.022; B = B.HCl = 0.05 | k AB | 30 | | 5.2 | −3 | | | ([3a]) |
| .15 | d-$CH_3C$<(CHCH$_2$ / COCH$_2$)>CHC<($CH_2$ / $CH_3$) + $NH_2NHC_6H_5$ (carvone) | Et 83 | A = 0.02; B = 0.14; B.HCl = 0.01 | k AB | 30 | | 3.7 | −4 | | | ([3a]) |
| .16 | d-$CH_3C$<(CHCH$_2$ / COCH$_2$)>CHC<($CH_2$ / $CH_3$) + $NH_2OH$ (carvone) | Et 83 | A = 0.065; B = B.HCl = 0.09 See Supplementary table | k AB | 30 | | 4.0 | −3 | | | ([3a]) |
| .17 | $C_6H_5CH{:}CHCHO$ + $NH_2NHCONH_2$ | CeW; b 1 | | k AB | 25 | | 1.13 | −1 | | * | ([5]) |
| | | b 2 | | " | " | | 1.11 | 0 | | | |
| .18 | $C_6H_5CHO$ + $NH_2NHCONH_2$ | $H_2O$; pH 7 | | k AB | 25 | | 3.4 | −2 | | * | ([1]) |
| | | CeW; b 1 | | k AB | 25 | | 8.5 | −2 | | * | ([5]) |
| | | b 2 | | | " | | 2.4 | 0 | | | |
| .19 | $C_6H_5CHO$ + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 0 | 540 | | | | | ([4]) |
| .20 | $C_6H_5CHO$ + l-$C_{10}H_{19}NH_2$ menthyl | $C_2H_5OH$ | | | 18 | 1920 | | | | | ([4]) |
| | | $C_6H_5CH_2OH$ | 0.05 | | " | 960 | | | | | |
| | | $O{:}(CH_2)_4{:}O$ | " | | " | 1860 | | | | | |
| | | $C_6H_5NO_2$ | " | | " | 4200 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 8600 | | | | | |
| | | $CHCl_3$ | " | | " | 27000 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^0 \times 10^n$ $k^0$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .21 | $C_6H_5COCH_3 + NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 2.04 | −4 | | | (3) |
| | | | | " | 25.0 | | 4.1 | −4 | 4.6 | | |
| | | CeW; b 1 | | $k$ AB | 25 | | 5.5 | −3 | | * | (5) |
| | | b 2 | | | " | | 4.7 | −2 | | | |
| | | | | See supplementary table (.13) | | | | | | | (1a) |
| .22 | $C_6H_5COCH_3 + NH_2NHC_6H_5 \cdot HCl$ | Et 75 | | | 0 | 10800 | | | | | (4) |
| .23 | $C_6H_5COCH_3 + NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 35 | 1440 | | | | | (4) |
| .24 | $p\text{-}CH_3C_6H_4COCH_3 + NH_2NHCONH_2$ | Et 83 | | See supplementary table (.13) | | | | | | | (1a) |
| .25 | $1,4\text{-}(CH_3)_2\text{-}C_6H_3\text{-}2\text{-}CHO + NH_2NHC_6H_5 \cdot HCl$ | Et 75 | | | 0 | 3000 | | | | | (4) |
| .26 | $1,4\text{-}(CH_3)_2\text{-}C_6H_3\text{-}2\text{-}CHO + NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 0 | 180 | | | | | (4) |
| .27 | $o\text{-}CH_3OC_6H_4CHO + NH_2NHC_6H_5 \cdot HCl$ | Et 75 | | | 0 | 60 | | | | | (4) |
| .28 | $o\text{-}CH_3OC_6H_4CHO + l\text{-}C_{10}H_{19}NH_2$ | $C_2H_5OH$ | | | 18 | 720 | | | | | (4) |
| | menthyl | $C_6H_5CH_2OH$ | 0.05 | | " | 840 | | | | | |
| | | $O:(CH_2)_4:O$ | " | | " | 1020 | | | | | |
| | | $C_6H_5NO_2$ | " | | " | 1080 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 4000 | | | | | |
| | | $CHCl_3$ | " | | " | 4115 | | | | | |
| .29 | $p\text{-}CH_3OC_6H_4CHO + NH_2NHCONH_2 \cdot HCl$ | Et 70 | A = 0.025; B = 0.050 | | 0 | 840 | | | | | (4) |
| | | | | See supplementary table (.13) | | | | | | | (1a) |

| No. | Reaction | Solvent (Medium | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .30 | $p$-$CH_3OC_6H_4CHO$ + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 0 | 3000 | | | | | ([4]) |
| .31 | $p$-$CH_3OC_6H_4CHO$ + $NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 0 | 900 | | | | | ([4]) |
| .32 | $p$-$CH_3OC_6H_4CHO$ + $l$-$C_{10}H_{19}NH_2$ | $C_2H_5OH$ | | | 18 | 4200 | | | | | ([4]) |
| | menthyl | $C_6H_5CH_2OH$ | 0.05 | | " | 4200 | | | | | |
| | | $O:(CH_2)_4:O$ | " | | " | 13800 | | | | | |
| | | $C_6H_5NO_2$ | " | | " | 30200 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 43000 | | | | | |
| | | $CHCl_3$ | " | | " | 174000 | | | | | |
| .33 | 1, 2-$(CH_3O)_2$-$C_6H_3$-3-CHO + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 0 | 720 | | | | | ([4]) |
| .34 | 1, 2-$(CH_3O)_2$-$C_6H_3$-4-CHO + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 0 | 11400 | | | | | ([4]) |
| .35 | $o$-$OHC_6H_4CHO$ + $l$-$C_{10}H_{19}NH_2$ | $O:(CH_2)_4:O$ | 0.05 | | 18 | 300 | | | | | ([4]) |
| | menthyl | $C_6H_5NO_2$ | " | | " | 540 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 420 | | | | | |
| | | $CHCl_3$ | " | | " | 3960 | | | | | |
| .36 | $p$-$OHC_6H_4CHO$ + $NH_2NHCONH_2.HCl$ | Et 70 | | | 0 | 900 | | | | | ([4]) |
| .37 | $p$-$OHC_6H_4CHO$ + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 0 | 12000 | | | | | ([4]) |
| .38 | $p$-$OHC_6H_4CHO$ + $NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 0 | 540 | | | | | ([4]) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .39 | $p$-$OHC_6H_4CHO$ + $l$-$C_{10}H_{19}NH_2$ menthyl | $C_2H_5OH$ | | | 18 | 4900 | | | | | (4) |
| | | $C_6H_5CH_2OH$ | 0.05 | | " | 2640 | | | | | |
| | | $O:(CH_2)_4:O$ | " | | " | 6000 | | | | | |
| | | $C_6H_5NO_2$ | " | | " | 2100 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 2600 | | | | | |
| | | $CHCl_3$ | " | | " | 7200 | | | | | |
| .40 | $o$-$OHC_6H_4COCH_3$ + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 35 | 12600 | | | | | (4) |
| .41 | $o$-$OHC_6H_4COCH_3$ + $NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 35 | 13800 | | | | | (4) |
| .42 | $p$-$OHC_6H_4COCH_3$ + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 35 | 19200 | | | | | (4) |
| .43 | $p$-$OHC_6H_4COCH_3$ + $NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 35 | 6600 | | | | | (4) |
| .44 | 1-OH-2-$CH_3O$-$C_6H_3$-4-CHO + $NH_2NHC_6H_5.HCl$ | Et 75 | | | 0 | 12000 | | | | | (4) |
| .45 | 1-OH-2-$CH_3O$-$C_6H_3$-4-CHO + $NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 0 | 600 | | | | | (4) |
| .46 | 1-OH-2-$CH_3O$-$C_6H_3$-4-CHO + $l$-$C_{10}H_{19}NH_2$ menthyl | $C_2H_5OH$ | | | 18 | 5300 | | | | | (4) |
| | | $C_6H_5CH_2OH$ | 0.05 | | " | 3300 | | | | | |
| | | $O:(CH_2)_4:O$ | " | | " | 17400 | | | | | |
| | | $C_6H_5NO_2$ | " | | " | 9300 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 6000 | | | | | |
| | | $CHCl_3$ | " | | " | 4300 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .47 | 1-OH-2-$CH_3O$-$C_6H_3$-6-CHO + $l$-$C_{10}H_{19}NH_2$ menthyl | O:$(CH_2)_4$:O | 0.05 | | 18 | 180 | | | | | |
| | | $C_6H_5NO_2$ | " | | " | 300 | | | | | |
| | | $C_6H_5CH_3$ | " | | " | 210 | | | | | |
| | | $CHCl_3$ | " | | " | 1320 | | | | | |
| .48 | 1-OH-3, 5-$(CH_3)_2$-$C_6H_2$-2-CHO + $NH_2NHC_6H_5$.HCl | Et 75 | | | 0 | 120 | | | | | (4) |
| .49 | 1-OH-3, 5-$(CH_3)_2$-$C_6H_2$-2-CHO + $NH_2OH$.HCl | Et 75 | A = 0.2; B = 0.1 | | 0 | 240 | | | | | (4) |
| .50 | 1-OH-3, 5-$(CH_3)_2$-$C_6H_2$-4-CHO + $NH_2NHC_6H_5$.HCl | Et 75 | | | 0 | 5100 | | | | | (4) |
| .51 | 1-OH-3, 5-$(CH_3)_2$-$C_6H_2$-4-CHO + $NH_2OH$.HCl | Et 75 | A = 0.2; B = 0.1 | | 0 | 7800 | | | | | (4) |
| .52 | o-$NO_2C_6H_4CHO$ + $NH_2NHCONH_2$ | CeW; b 1 | | $k$ AB | 25 | | 2.7 | -2 | | * | (5) |
| | | b 2 | | " | " | | 1.3 | 0 | | | |
| .53 | o-$BrC_6H_4CHO$ + $NH_2NHC_6H_5$.HCl | Et 75 | | | 0 | 300 | | | | | (4) |
| .54 | p-$BrC_6H_4CHO$ + $NH_2NHC_6H_5$.HCl | Et 75 | | | 0 | 1140 | | | | | (4) |
| .55 | p-$BrC_6H_4CHO$ + $NH_2OH$.HCl | Et 75 | A = 0.2; B = 0.1 | | 0 | 120 | | | | | (4) |
| .56 | p-$ClC_6H_4COCH_3$ + $NH_2NHCONH_2$ | Et 83 | | See Supplementary table (.13) | | | | | | | (1a) |
| .57 | p-$BrC_6H_4COCH_3$ + $NH_2NHCONH_2$ | Et 83 | | " | " | " | " | | | | (1a) |
| .58 | α-$C_{10}H_7CHO$ + $NH_2NHC_6H_5$.HCl | Et 75 | | | 0 | 11700 | | | | | (4) |
| .59 | α-$C_{10}H_7CHO$ + $NH_2OH$.HCl | Et 75 | A = 0.2; B = 0.1 | | 0 | 300 | | | | | (4) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Defined mass-action law | Temperature | Half-time | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .60 | 1-OH-$C_{10}H_6$-4-CHO + $NH_2OH.HCl$ | Et 75 | A = 0.2; B = 0.1 | | 0 | 7200 | | | | | (4) |
| .61 | $C_4H_3OCHO$ + $NH_2NHCONH_2$ | $H_2O$; pH 7 | | $k$ AB | 0.0 | | 6.5 | -2 | | * | (1) (3) |
| | furfural | | | | 25.0 | | 1.2 | -1 | 4.1 | | |
| | | CeW; b 1 | | $k$ AB | 25 | | 2.7 | -2 | | * | (5) |
| | | b 2 | | " | " | | 9.7 | -1 | | | |

## SOLVENTS

(1) 0.07 $Na_2HPO_4$ + 0.03 $NaH_2PO_4$; pH = 7

(2) Phosphate buffers; selected points

(4) Et 75 = $C_2H_5OH$ 75 vol % + $H_2O$ 25 vol %

(5) CeW = $CH_3OCH_2CH_2OH$ (cellosolve) 60 % + $H_2O$ 40 %

b 1 = basic $CH_3COONa$ buffer solution

b 2 = 0.02 ($CH_2ClCOOH$ + $CH_2ClCOONa$) buffer, corresponding to maximum rate

## COMMENTS

(.1) From reverse reaction and equilibrium. (.3) Heats of activation $\Delta H_a$ given. For reaction (.53), very good agreement between the values of $k$ of (1) and (3) in $H_2O$ at pH 7. (.5) The reactions with $NH_2NHCONH_2$ are acid catalyzed. In chloroacetate buffers, there is a downward trend of $k$ as the reaction progresses.

## SUPPLEMENTARY TABLES

(.13) $ArCOCH_3$ + $NH_2NHCONH_2$ Solvent Et 83 (1a)

The rate constant $k = Ae^{-E/RT}$, defined as first-order, is won by comparison with the rate of reaction (.13), *d*-carvone + $NH_2NHCONH_2$, at equal concentrations of the reactants. The tables give $A$ ($sec^{-1}$) and $E$ (kcal) (30 - 50° C).

## SUPPLEMENTARY TABLES *(continued)*

(.13) *(continued)*

| $ArCOCH_3$ | $A$ | $E$ |
|---|---|---|
| $C_6H_5COCH_3$ | 3.6 | 7.8 |
| $p$-$CH_3C_6H_4COCH_3$ | 0.4 | 6.5 |
| $p$-$CH_3OC_6H_4COCH_3$ | 0.0045 | 4.0 |
| $p$-$ClC_6H_4COCH_3$ | 460 | 10.3 |
| $p$-$BrC_6H_4COCH_3$ | 1670 | 11.0 |

(.14) (.15) (.16) General acid catalysis (at constant pH)

| Reaction | | Buffer | | $k$ |
|---|---|---|---|---|
| (.14) | Formic acid | 0.076 + Formate | 0.074 | $9.2 \times 10^{-3}$ |
| | | 0.114 | 0.111 | $1.0 \times 10^{-2}$ |
| | | 0.152 | 0.148 | $1.1 \times 10^{-2}$ |
| (.15) | Acetic acid | 0.0128 + Acetate | 0.0112 | $3.3 \times 10^{-4}$ |
| | | 0.0256 | 0.0223 | $5.8 \times 10^{-4}$ |
| | | 0.0384 | 0.0335 | $7.8 \times 10^{-4}$ |
| (.16) | Hydrogen maleate | 0.032 + Maleate | 0.032 | $3.0 \times 10^{-3}$ |
| | | 0.048 | 0.048 | $3.5 \times 10^{-3}$ |
| | | 0.064 | 0.064 | $3.8 \times 10^{-3}$ |

## LITERATURE

(1) J.B.Conant, P.D.Bartlett, *ACS* 1932, **54**, 2881. (1a) R.P. Cross, P. Fugassi, *ACS* 1949, **71**, 223. (2) A.Ölander, *ZPC*[A] 1927, **129**, 1. (3) F.P.Price, L.P.Hammett, *ACS* 1941, **63**, 2387. (3a) G.H.Stempel,Jr., G.S.Schaffel, *ACS* 1944, **66**, 1158. (4) G.Vavon, P.Montheard, *BCF*, 1940, **7**, 551, 560. (5) F.H.Westheimer, *ACS* 1934, **56**, 1962.

# CONDENSATION

## Aliphatic alcohol + Alkyl halide

*Liquid phase*

Reaction type $ROH + R'X \rightarrow ROR' + HX$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Medium (Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3OH + (C_6H_5)_3CCl$ | $C_6H_6$ | A = 0.03 - 0.19 | $C_5H_5N$ | 0.1 | $k A^2B$ | 25 | 4.34 | -3 | 6.6 | * | (4) |
| | | | B = 0.1 | $\alpha$-$CH_3C_9H_6N$ | " | " | " | 3.50 | -3 | (25° - 60°) | | |
| | | | | $C_9H_7N$ | " | " | " | 5.84 | -3 | | | |
| | | | | $C_6H_5N(C_2H_5)_2$ | " | " | " | 4.17 | -3 | | | |
| | $CH_3OH + (C_6H_5)_3CCl (+ C_6H_5OH)$ | " | " | $C_5H_5N$ | 0.1 | $k ABC$ | 25 | 3.14 | -2 | 6.6 | * | (4) |
| | | | | | 0.2 | " | " | 2.0 | -2 | (25° - 60°) | | |
| | | | | $\alpha$-$CH_3C_9H_6N$ | " | " | " | 3.34 | -2 | | | |
| .2 | $CH_3OH + (C_6H_5)_3CCl (+ p\text{-}NO_2C_6H_4OH)$ | " | " | $C_5H_5N$ | 0.1 | $k ABC$ | 25 | ~ 8 | -2 | 6.6 (25° - 60°) | * | (4) |
| .3 | $CH_3OH + (C_6H_5)_3CBr$ | $C_6H_6$ | A = 0.03 - 0.19 | $C_5H_5N$ | 0.1 - 0.2 | $k A^2B$ | 25 | ~ 3.7 | -1 | 6.6 | * | (4) |
| | | | B = 0.1 | $Et_3N$ | " | " | " | ~ 3 | -1 | (25° - 60°) | | |
| | $CH_3OH + (C_6H_5)_5CBr (+ C_6H_5OH)$ | " | " | $C_5H_5N$ | 0.1 | $k ABC$ | 25 | ~ 3 | 0 | 6.6 | * | (4) |
| .4 | $CH_3OH + p\text{-}[(CH_3)_3CC_6H_4]_3Cl$ | $C_6H_6$ | A = 0.03 - 0.19 | $C_5H_5N$ | 0.09 | $k A^2B$ | 25 | ~ 1.3 | -1 | 6.6 | * | (4) |
| | | | B = 0.1 | | | | | | | (25° - 60°) | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $C_2H_5ONa + CH_3I$ | $C_2H_5OH$ | A = 1 | | | $k$ AB | 0 | 2.8 | -5 | | | (2) |
| | | | B = 0.5 - 2 | | | | 6 | 5.9 | -5 | | | |
| | | | | | | | 12 | 1.2 | -4 | | | |
| | | | | | | | 18 | 2.4 | -4 | | | |
| | | | | | | | 24 | 5.0 | -4 | | | |
| | | | | | | | 30 | 1.0 | -3 | | | |
| .6 | $C_4H_9S^- + C_4H_9Br$ | $CH_3OH$ | A = B = 0.10 | | | $k$ AB | 25 | 7.34 | -5 | | * | (3) |
| | | | | | | | 35 | 1.83 | -4 | | | |
| | | | | | | | 45 | 3.33 | -4 | | | |
| | | $C_2H_5OH$ | A = B = 0.05 | | | " | 25 | 3.33 | -4 | | | |
| | | | | | | | 35 | 8.5 | -4 | | | |
| | | | | | | | 45 | 1.48 | -3 | | | |
| | | " | 0.10 | | | " | 25 | 3.0 | -4 | | | |
| | | | | | | | 35 | 8.0 | -4 | | | |
| | | | | | | | 45 | 1.46 | -3 | | | |
| | | " | 0.20 | | | " | 25 | 3.0 | -4 | | | |
| | | | | | | | 35 | 7.5 | -4 | | | |
| | | | | | | | 45 | 1.27 | -3 | | | |
| .7 | $C_6H_5CH_2O^- + CH_3I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 2.65 | -3 | | * | (1) |
| | | | | | | | 40 | 8.75 | -3 | 21.6 | | |
| .8 | $C_6H_5CH_2O^- + C_2H_5I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 2.37 | -4 | | * | (1) |
| | | | | | | | 40 | 7.82 | -4 | 21.6 | | |
| .9 | $C_6H_5CH_2O^- + C_3H_7I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 9.26 | -5 | | * | (1) |
| | | | | | | | 40 | 3.06 | -4 | 21.6 | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .10 | $C_6H_5CH_2O^- + (CH_3)_2CHI$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 5.50 | -5 | | * | (1) |
| | | | | | | | 40 | 1.81 | -4 | 21.6 | | |
| .11 | $C_6H_5CH_2O^- + C_4H_9I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 6.67 | -5 | | * | (1) |
| | | | | | | | 40 | 2.20 | -4 | 21.6 | | |
| .12 | $C_6H_5CH_2O^- + (CH_3)_2CH_2CH_2I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 8.68 | -5 | | * | (1) |
| | | | | | | | 40 | 2.86 | -4 | 21.6 | | |
| .13 | $C_6H_5CH_2O^- + (CH_3)_2CH_2CH_2CH_2I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 3.33 | -5 | | * | (1) |
| | | | | | | | 40 | 1.10 | -4 | 21.6 | | |
| .14 | $C_6H_5CH_2O^- + C_4H_9CH(CH_3)I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 9.67 | -5 | | * | (1) |
| | | | | | | | 40 | 3.19 | -4 | 21.6 | | |
| .15 | $C_6H_5CH_2O^- + C_7H_{15}I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 6.67 | -5 | | * | (1) |
| | | | | | | | 40 | 2.20 | -4 | 21.6 | | |
| .16 | $C_6H_5CH_2O^- + C_8H_{17}I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 6.67 | -5 | | * | (1) |
| | | | | | | | 40 | 2.20 | -4 | 21.6 | | |
| .17 | $C_6H_5CH_2O^- + C_6H_{13}CH(CH_3)I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 7.25 | -5 | | * | (1) |
| | | | | | | | 40 | 2.40 | -4 | 21.6 | | |
| .18 | $C_6H_5CH_2O^- + C_{16}H_{33}I$ | $C_2H_5OH$ | 0.1 | | | $k$ AB | 30 | 6.84 | -5 | | * | (1) |
| | | | | | | | 40 | 2.26 | -4 | 21.6 | | |
| .19 | $(C_6H_5)_3COH + (C_6H_5)_3CBr$ | $C_6H_5$ | A = 0.03 - 0.19<br>B = 0.1 | $C_5H_5N$ | 0.1 | $k A^2B$ | 60 | 2.3 | -5 | 6.6<br>(25° - 60°) | * | (4) |



942151 O—51——16

## COMMENTS

([4]) (.1) (.2) (.3) (.4) (.19) Mechanism assumed to be $2A + RX \rightarrow A_2RX$ ( rate determining ) ; $A_2RX \rightarrow R^+ + X^- + 2A$(fast); $R^+ + A \rightarrow$ ether $+ H^+$(fast). The rate determining step gives the third-order law $kA^2B$. In the presence of phenol, one molecule of the latter replaces one molecule of A, hence the third-order law $kABC$. The phenol undergoes no change in the overall reaction. ([3]) (.6) Some decrease of $k$ with increasing ionic strength. ([1]) (.7) - (.18) Rate law and values of $k$ valid only at the given concentration.

## LITERATURE

([1]) P.C.Haywood, *CSL* 1922, **121**, 1904. ([2]) W.Hecht, M.Conrad, *ZPC* 1889, **3**, 450.

([3]) O.R.Quayle, E.E.Royals, *ACS* 1942, **64**, 226. ([4]) C.G.Swain, *ACS* 1948, **70**, 1119.

# CONDENSATION

## Phenol + Alkyl halide

Reaction type $ArOH + RX \rightarrow ArOR + HX$

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5O^- + C_4H_9Br$ | $CH_3OH$ | 0.10 | | | $k$AB | 25 | 6.67 | -8 | | | ([1]) |
| | | | | | | | 35 | 2.17 | -7 | | | |
| | | | | | | | 45 | 5.84 | -7 | 23 | | |
| | | $C_2H_5OH$ | 0.05 | | | $k$AB | 25 | 2.19 | -7 | | | |
| | | | | | | | 35 | 6.50 | -7 | | | |
| | | | | | | | 45 | 1.35 | -6 | | | |
| | | | 0.10 | | | " | 25 | 1.66 | -7 | | | |
| | | | | | | | 35 | 5.33 | -7 | | | |
| | | | | | | | 45 | 1.35 | -6 | 23 | | |
| | | | 0.20 | | | " | 25 | 1.45 | -7 | | | |
| | | | | | | | 35 | 4.67 | -7 | | | |
| | | | | | | | 45 | 1.12 | -6 | | | |
| .2 | $C_6H_5S^- + C_4H_9Br$ | $CH_3OH$ | 0.10 | | | $k$AB | 25 | 7.5 | -5 | | * | ([1]) |
| | | | | | | | 35 | 1.8 | -4 | | | |
| | | | | | | | 45 | 3.76 | -4 | 17.8 | | |
| | | $C_2H_5OH$ | 0.05 | | | $k$AB | 25 | 2.17 | -4 | | | |
| | | | | | | | 35 | 5.68 | -4 | | | |
| | | | | | | | 45 | 1.10 | -3 | 17.4 | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $C_6H_5S^- + C_4H_9Br$ (*continued*) | | 0.10 | | | $k$ AB | 25 | 2.09 | -4 | | | |
| | | | | | | | 35 | 5.18 | -4 | | | |
| | | | | | | | 45 | 9.18 | -4 | 15.7 | | |
| | | | 0.20 | | | $k$ AB | 25 | 2.0 | -4 | | | |
| | | | | | | | 35 | 4.66 | -4 | | | |
| | | | | | | | 45 | 7.91 | -4 | 14.1 | | |
| | | $C_6H_6$ | 0.10 | | | $k$ AB | 35 | 2.0 | -5 | | | |
| .3 | $C_6H_5OH + (C_6H_5)_3CCl$ | $C_6H_6$ | A = 0.03 - 0.19<br>B = 0.1 | $C_5H_5N$ | 0.1 | $k A^2B$ | 25 | 6.7 | -6 | 6.6<br>(25°-60°) | * | ([2]) |
| .4 | $C_6H_5OH + (C_6H_5)_3CBr$ | $C_6H_6$ | A = 0.03 - 0.19<br>B = 0.1 | $C_5H_5N$ | 0.07<br>0.22 | $k A^2B$ | 25<br>25 | 6.7<br>3.0 | -5<br>-3 | 6.6<br>(25°-60°) | * | ([2]) |
| .5 | $p - NO_2C_6H_4OH + (C_6H_5)_3CBr$ | $C_6H_6$ | A = 0.03 - 0.19<br>B = 0.1 | $C_5H_5N$ | 0.055<br>0.110 | $k A^2B$ | 25<br>25 | 1.3<br>2.8 | -2<br>-3 | 6.6<br>(25°-60°) | * | ([2]) |

## COMMENTS

(.2) Some decrease of $k$ with increasing ionic strength. The reaction in $C_2H_5OH$ is retarded by LiCl.

(.3) (.4) (.5) The mechanism accounting for the third-order rate law is assumed to be 2 ArOH + RX $\longrightarrow$ $(ArOH)_2RX$ (rate determining); $(ArOH)_2RX \longrightarrow R^+ + X^- + 2$ ArOH (fast); ArOH + $R^+ \longrightarrow$ ArOR + $H^+$ (fast).

## LITERATURE

([1]) O.R. Quayle, E.E. Royals, *ACS* 1942, **64**, 226. ([2]) C.G. Swain, *ACS* 1948, **70**, 1119.

# SOLVOLYSIS

## Ethers

*Liquid phase*

Reaction type $ROR' + H_2O \rightarrow ROH + R'OH$

Amounts are in M/l.

Rates in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_5OC_2H_5 + H_2O$ | $H_2O$ | 0.48 | X = $p$-$CH_3C_6H_4SO_3H$ | 0.5 | $k$AX | 25 | (2.44) | -13 | | | | * | (1) |
| | | | | | | | 65 | 7.24 | -10 | 36.4 | 3.3 | 14 | | |
| | | | | | | | 75 | 3.33 | -9 | 34.6 | 2.2 | 13 | | |
| | | | | | | | 85 | 1.30 | -8 | 32.7 | 3.3 | 12 | | |
| | | | | | | | 95 | 4.38 | -8 | 30.8 | 1.1 | 7 | | |
| | | | | | | | 125 | (7.85) | -8 | | | | | |
| .2 | $(CH_3)_2CHOC_2H_5 + H_2O$ | $H_2O$ | 0.48 | X = $p$-$CH_3C_6H_4SO_3H$ | 0.5 | $k$AX | 25 | 2.50 | -12 | | | | * | (1) |
| | | | | | | | 55 | 1.21 | -9 | 37.8 | 2.2 | 16 | | |
| | | | | | | | 65 | 6.42 | -9 | 36.3 | 2.2 | 15 | | |
| | | | | | | | 75 | 3.04 | -8 | 34.8 | 2.7 | 14 | | |
| | | | | | | | 85 | 1.17 | -7 | 31.8 | 3.3 | 11 | | |
| | | | | | | | 125 | 8.38 | -6 | | | | | |
| .3 | $(CH_3)_2CHOCH(CH_3)_2 + H_2O$ | $H_2O$ | 0.48 | X = $p$-$CH_3C_6H_4SO_3H$ | 0.5 | $k$AX | 25 | 1.10 | -11 | | | | * | (1) |
| | | | | | | | 55 | 5.20 | -9 | 37.1 | 2.7 | 16 | | |
| | | | | | | | 65 | 2.67 | -8 | 35.3 | 2.2 | 15 | | |
| | | | | | | | 75 | 1.18 | -8 | 33.4 | 1.3 | 14 | | |
| | | | | | | | 85 | 4.37 | -7 | 31.5 | 8.5 | 12 | | |
| | | | | | | | 125 | 2.14 | -5 | | | | | |

## COMMENTS

(.1) (.2) (.3) Converted to seconds from original $k$ in minutes. Arrhenius law not obeyed, $E$ and $A$ vary with the temperature. Empirical formulas ( $k$ in $min^{-1}$ ) (.1) $\log k = ( - 14535/T ) - 0.057476T + 55.069$; (.2) $\log k = ( - 13456/T ) - 0.048120T + 49.6355$; (.3) $\log k = ( - 14592/T ) - 0.060150T + 57.711$. Values of $k$ at 25° and at 125°C extrapolated with the aid of the above formulas. The rates of hydrolysis of these ethers are exceedingly slow; that of $C_2H_5OC_2H_5$ is, roughly, $10^{16}$ slower than hydrolysis of $CH_3COOC_2H_5$. The half-time of the hydrolysis of $C_2H_5OC_2H_5$ in 1*M* solution is 90300 years.

## LITERATURE

A. Skrabal, A. Zahorka, *MHC* 1933, **63**, 1.

# SOLVOLYSIS

## Acetals



Reaction type $R_1R_2C(OR)_2 + H_2O \longrightarrow R_1R_2CO + 2\ ROH$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCH(OC_3H_7)_2 + H_2O$ | $H_2O$ | Sat $C_6H_5COOH$ + NaCl | | 0.00 | $kA[H^+]$ | 25 | 1.04 | -1 | | * | ([3]) |
| | | | | | 0.008 | | " | 1.09 | -1 | | | |
| | | | | | 0.10 | | " | 1.29 | -1 | | | |
| | | | | | 0.40 | | " | 1.80 | -1 | | | |
| | | | | | 1.00 | | " | 2.96 | -1 | | | |
| | | | | HCl 0.01 + NaCl | 0.0 | " | 25 | 1.08 | -1 | | | " |
| | | | | | 0.60 | | " | 2.1 | -1 | | | |
| | | | | | 2.00 | | " | 7.2 | -1 | | | |
| | | | | KCl | 1.0 | " | " | 2.8 | -1 | | | |
| | | | | KBr | 1.0 | | " | 3.8 | -1 | | | |
| | | | | KI | 1.0 | | " | 5.3 | -1 | | | |
| | | | | HCl 0.5 + NaCl | 0.0 | " | " | 1.77 | -1 | | | " |
| | | | | | 0.80 | | " | 3.64 | -1 | | | |
| .2 | $CH_3CH(OCH_3)_2 + H_2O$ | $H_2O$ | Sat $C_6H_5COOH$ + NaCl | | 0.00 | $kA[H^+]$ | 25 | 2.74 | -1 | | | ([3]) |
| | | | | | 0.02 | | " | 2.84 | -1 | | | |
| | | | | | 0.08 | | " | 3.10 | -1 | | | |
| | | | | | 0.56 | | " | 4.75 | -1 | | | |
| | | | | | 2.00 | | " | 1.30 | 0 | | | |
| | | | | | 3.00 | | " | 2.65 | 0 | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $CH_3CH(OC_2H_5)_2 + H_2O$ | $H_2O$ | 0.01 | $H^+$ | 0.001 | $kA[H^+]$ | 25 | 1.35 | 0 | | | (6) |
| | | $H_2O$ | Sat $C_6H_5COOH$ + NaCl | | 0.00 | $kA[H^+]$ | 25 | 1.32 | 0 | | | (3) |
| | | | | | 0.04 | | " | 1.36 | 0 | | | |
| | | | | | 0.10 | | " | 1.56 | 0 | | | |
| | | | | | 0.40 | | " | 1.84 | 0 | | | |
| | | | | | 0.50 | | " | 1.94 | 0 | | | |
| | | | | | 1.00 | | " | 2.92 | 0 | | | |
| | | | Sat $C_6H_5COOH$ + $C_6H_5COONa$ | | 0.40 | " | " | | | | | " |
| | | $H_2O$ | | + NaCl | 0.00 | | " | 1.48 | 0 | | | |
| | | | | | 0.40 | | " | 2.17 | 0 | | | |
| | | | | | 1.00 | | " | 3.46 | 0 | | | |
| | | | | | 2.10 | | " | 7.66 | 0 | | | |
| | | | | | 2.74 | | " | 1.19 | +1 | | | |
| | | $H_2O$ | | HCl | 0.001 | $kA$ | 15(?) | 3.16 | -4 | | | (2) |
| | | | | $(COOH)_2$ | 0.01 | | | 5.5 | -4 | | | |
| | | | | HCOOH | 0.0104 | | | 7.6 | -5 | | | |
| | | | | $CH_3COOH$ | 0.0096 | | | 1.1 | -5 | | | |
| | | $D_2O$ | | HCl | 0.001 | " | " | 8.4 | -4 | | | " |
| | | | | $(COOH)_2$ | 0.01 | | | 1.40 | -3 | | | |
| | | | | HCOOH | 0.0104 | | | 7.5 | -5 | | | |
| | | | | $CH_3COOH$ | 0.0096 | | | 1.06 | -5 | | | |
| .4 | $CH_3CH(OC_4H_9)_2 + H_2O$ | $H_2O$ | 0.02 | HCl | 0.007 | $kAB$ | 25 | 1.27 | 0 | | | (4) |
| | | | | | | | 35 | 4.44 | 0 | 22.7 | | |
| | | Dx 60 | 0.02 | HCl | 0.007 | $kAB$ | 15 | 2.11 | -2 | | | " |
| | | | | | | | 25 | 7.99 | -2 | 22.7 | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $(CH_3)_2C(OCH_3)_2 + H_2O$ | $H_2O$, buffers | ~ 0.1 | $H^+$ | $1.0 \times 10^{-7}$<br>$2.0 \times 10^{-7}$ | $kA[H^+]$ | 25<br>" | 6.4<br>5.7 | -2<br>-2 | | * | (5) |
| .6 | $(CH_3)_2C(OC_2H_5)_2 + H_2O$ | $H_2O$, buffers | ~ 0.1 | $H^+$ | $2.0 \times 10^{-7}$ | $kA[H^+]$ | 25 | 2.3 | -3 | | * | (5) |

## SOLVENTS

Dx 60 = $H_2O$ + 60 vol % dioxane (4).

## COMMENTS

**Methods.** (2) interferometric; (3) dilatometric. **Reactions.** (.1) Selected points. Original (3) gives $k$ in HCl solutions under the erroneous heading "$k \times 10^3$;" it should evidently read "$k$". The original data of (3) have been converted to sec and ln. (.2) Further data in the presence of $C_6H_5COOH + C_6H_5COONa + NaCl$ in original (3). (.3) Data of (2): no indication of the temperature, but from the context it appears that it is 15° C. If so, extrapolation to 25°C gives a catalytic constant, defined by $kA[H^+]$, in fair agreement with (3).

## LITERATURE

(1) P.P. Bell, W.C.E. Higginson, Proc. Roy. Soc., 1949, A197, 141. (2) J.C. Hornel, J.A.V. Butler, *CSL* 1936, 1361. (3) A. R. Olson, L.K.J. Tong, *ACS* 1944 **66**, 1555. (4) F.N. Prilezhaeva, F.S. Shapiro, M.F. Shostakovskii, *ZOK* 1948, **18**, 1663. (5) A. Skrabal, F. Bilger, *ZPC* 1927, **130**, 29. (6) L.K.J. Tong, A.R. Olson, *ACS* 1943, **65**, 1704.

# SOLVOLYSIS

## Acid anhydrides

*Liquid phase*

Reaction type $Ac_2O + H_2O \rightarrow 2\ AcOH$

Amounts are in M/l.

Rates in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3CO)_2O + H_2O$ | $H_2O$ | A = 0.5 | | | $kA$ | 0 | 4.7 | -4 | * | (1) |
| | | | | | | | 15 | 1.2 | -3 | | |
| | | $H_2O$ | A = 0.02 | | | $kA$ | 25 | 2.7 | -3 | * | (3) |
| | | | 0.116 | | | | " | 2.6 | -3 | | |
| | | | 0.235 | | | | " | 2.7 | -3 | | |
| | | | 0.735 | | | | " | 2.4 | -3 | | |
| | | | 1.070 | | | | " | 2.2 | -3 | | |
| | | $H_2O + CH_3COOH$ % | A = 0.08; B = 0.18 | | | $kA$ | | | | | (1) |
| | | 50 | | | | | 15 | 2.7 | -4 | | |
| | | 80 | | | | | " | 9.4 | -5 | | |
| | | 90 | | | | | " | 4.7 | -5 | | |
| | | $CH_3COOH$ | A = 0.08; B = 0.18 | | | $kAB$ | 15 | 7.0 | -6 | | " |
| | | $(CH_3)_2CO$ | A = 10; B = 1.8 | | | $kAB$ | 15 | 1.2 | -6 | | |
| | | $H_2O + CH_3COOH$ 90% | A = 0.08; B = 0.18 | | | $kA$; $k'A[H_2SO_4]$ | | | | | " |
| | | | | $H_2SO_4$ | 0 | | 15 | 4.7 | -5 | | |
| | | | | | 0.0166 | | $k$ | 1.8 | -5 | | |
| | | | | | " | | $k'$ | 1.1 | -2 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3CO)_2O + H_2O$ (*continued*) | | | | 0.033 | | $k$ | 3.3 | -4 | | |
| | | | | | " | | $k'$ | 1.0 | -2 | | |
| | | | | | 0.05 | | $k$ | 5.8 | -4 | | |
| | | | | | " | | $k'$ | 1.2 | -2 | | |
| | | | | | 0.1 | | $k$ | 1.3 | -3 | | |
| | | | | | | | $k'$ | 1.3 | -2 | | |
| | | A = 62g; B = 1.12g; $CH_3COOH$ = 267g | | | | $k$ AB | 70.1 | 6.0 | -5 | * | ([2]) |
| | | | | | | | 80.5 | 1.05 | -4 | | |

## COMMENTS

Date of ([3]), converted to the base *e* from decimal log, are consistent with those of ([1]). Only one composition in ([2]) (preliminary communication).

## LITERATURE

([1]) K.J.P.Orton, M.Jones, *CSL* 1912, **101**, 1708. ([2]) J.C.Phillip, *CSL* 1912, **28**, 259. ([3]) A.C.D.Rivett, N.V.Sidgwick, *CSL* 1910, **97**, 732.

# SOLVOLYSIS

## C : N bond

*Liquid phase*

Reaction type $R_1R_2C{:}NR + H_2O \rightarrow R_1R_2CO + H_2NR$

Amounts are in M/l.

Rates in M/l per sec.

| No. | Reaction | Medium (Solvent) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3)_2C{:}NOH + H_2O$ | $H_2O$; pH 1.22 | $k$A | 17 - 19 | 4.0 | -4 | | * | (2) |
| | | 1.70 | | | 7.5 | -4 | | | |
| | | 2.15 | | | 1.0 | -3 | | | |
| | | 2.58 | | | 9.2 | -4 | | | |
| | | 3.15 | | | 5.9 | -4 | | | |
| | | 4.25 | | | 9.0 | -5 | | | |
| | | 5.27 | | | 1.7 | -5 | | | |
| .2 | $CH_3CH{:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$AB | 25 | 1.73 | -4 | | * | (1) |
| .3 | $(CH_3)_2C{:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$A | 0.0 | 5.11 | -5 | | * | (3) |
| | | | | 25.1 | 2.78 | -4 | 11.0 | | |
| .4 | $COOH.C(CH_3){:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$AB | 25 | 6.3 | -7 | | * | (1) |
| .5 | $(C_2H_5)_2C{:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$A | 0.0 | 6.09 | -5 | | * | (3) |
| | | | | 25.0 | 2.26 | -4 | 8.5 | | |

| No. | Reaction | Medium (Solvent) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .6 | $(CH_3)_3CCH{:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$AB | 25 | 6.2 | −6 | | * | (1) |
| .7 | $(CH_3)_3CC(CH_3){:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$AB | 25 | 1.4 | −5 | | * | (1) |
| .8 | $\underbrace{CH_2(CH_2)_4}C{:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$A | 0.0<br>25.1 | 2.23<br>1.06 | −4<br>−3 | <br>10.1 | * | (3) |
| .9 | $C_6H_5CH{:}NNHCONH_2 + H_2O$ | $H_2O$; pH 7 | $k$AB | 25 | 1.0 | −7 | | * | (1) |

## COMMENTS

(1) Buffer solution 0.07 $Na_2HPO_4$ + 0.03 $NaH_2PO_4$. Rate constants $k$ from the rates of the reverse reaction and equilibrium constant. (2) Phosphate buffers. (3) From reverse reaction and equilibrium constant.

## LITERATURE

(1) J.B.Conant, P.D.Bartlett, *ACS* 1932, **54**, 2881. (2) A.Olander, *ZPC*[A] 1927, **129**, 1. (3) F.P.Price, L.P.Hammett, *ACS* 1941, **63**, 2387.

# SOLVOLYSIS

## CO - $NH_2$ bond (Acyl amide solvolysis)

*Liquid phase*

Reaction types

$$RCONH_2 + H_2O \rightarrow RCOO^- + NH_4^+$$

$$RCONH_2 + OH^- \rightarrow RCOO^- + NH_3$$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $k A[H^+]$ | 42.1 | 8.8 | -4 | | * | ([2]) |
| | | | | | | | 63.2 | 5.8 | -3 | | | |
| | | | | | | | 70.3 | 1.1 | -2 | | | |
| | | | | | | | 80.7 | 2.1 | -2 | 19.1 | | |
| | | $H_2O$ | 0.05 - 0.8 | HCl | 2 | $k A$ | 25 | 2.3 | -4 | | | ([7]) |
| | | | | | 4 | | " | 4.4 | -4 | | | |
| | | | | | 6 | | " | 5.1 | -4 | | | |
| | | | | | 8 | | " | 4.5 | -4 | | | |
| | | | | | 9.5 | | " | 3.5 | -4 | | | |
| | | | | $H_2SO_4$ | 1 | " | " | 3.0 | -4 | | | ([7]) |
| | | | | | 1.75 | | " | 4.5 | -4 | | | |
| | | | | | 2.25 | | " | 4.8 | -4 | | | |
| | | | | | 3 | | " | 4.3 | -4 | | | |
| | | | | | 4 | | " | 3.1 | -4 | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3CONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $kA[H^+]$ | 42.1 | 4.43 | -5 | | * | (2) |
| | | | | | | | 63.2 | 3.60 | -4 | | | |
| | | | | | | | 70.8 | 6.83 | -4 | | | |
| | | | | | | | 80.7 | 1.48 | -3 | 20.7 | | |
| | | $H_2O$ | 0.05 - 0.8 | HCl | 1.50 | $kA$ | 25 | 6.9 | -6 | | * | (7) |
| | | | | | 2.91 | | " | 1.08 | -5 | | | |
| | | | | | 4.13 | | " | 9.7 | -5 | | | |
| | | | | | 5.00 | | " | 7.2 | -5 | | | |
| | | | | $H_2SO_4$ | 0.49 | | " | 6.7 | -6 | | | " |
| | | | | | 1.25 | | " | 9.2 | -6 | | | |
| | | | | | 2.07 | | " | 7.5 | -6 | | | |
| | | $H_2O$ | ~ 0.15 | HCl | 1.0 | $kA$ | 18 | 3.4 | -6 | | * | (8) |
| | | | | | | | 25 | 6.4 | -6 | | | |
| | | | | | 0.5 | | 25 | 2.8 | -6 | | | " |
| | | $H_2O$ | ~ 0.15 | HCl | 0.5 - 1.0 | $kA[H^+]$ | 25 | 6.0 | -6 | | * | (8) |
| | | $H_2O$ | 0.166 | HCl | = B | $kA[H^+]$ | 65 | 5.0 | -4 | | * | (1) |
| | | | 0.333 | | | | " | 4.1 | -4 | | | |
| | | | 0.666 | | | | " | 3.8 | -4 | | | |
| | | | 1.333 | | | | " | 3.4 | -4 | | | |
| | | $H_2O$ | 0.1 | HCl | ~ A | $kA[H^+]$ | 49.3 | 1.28 | -4 | | * | (5) |
| | | | | | | | 64.3 | 3.71 | -4 | 15.4 | | |
| | | $H_2O$ | | pH | 1.04 | $kA[H^+]$ | 50 | 1.24 | -4 | | * | (4) |
| | | | | | 0.76 | | " | 1.19 | -4 | | | |
| | | | | | 0.59 | | " | 1.17 | -4 | | | |
| | | | | | 0.30 | | " | 1.02 | -4 | | | |
| | | | | | 0.05 | | " | 9.20 | -5 | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3CONH_2 + H_2O$ *(continued)* | | | | -0.15 | | 50 | 7.98 | -5 | | | |
| | | | | | -0.30 | | " | 6.93 | -5 | | | |
| | | | | | -0.45 | | " | 4.96 | -5 | | | |
| | | | | | -0.58 | | " | 3.72 | -5 | | | |
| | | $H_2O$ | 0.05 | $H_2SO_4$ | 2 | $k$ A | 25 | 9.92 | -6 | | * | (12) |
| | | | | " | 2.5 | | " | 1.10 | -5 | | | |
| | | | | HCl | 3 | | " | 1.00 | -5 | | | |
| | | | | " | 4 | | " | 8.55 | -6 | | | |
| | | | | " | 5 | | " | 6.02 | -6 | | | |
| | | | | HBr | 4 | | " | 6.72 | -6 | | | |
| | | | | " | 5 | | " | 5.44 | -6 | | | |
| | | | | HCl4 + LiCl1 | | | " | 8.51 | -6 | | | " |
| | | | | " NaCl1 | | | " | 9.81 | -6 | | | |
| | | | | " KCl1 | | | " | 9.70 | -6 | | | |
| | | | | HBr4 + LiBr1 | | | " | 5.99 | -6 | | | |
| | | | | " NaBr1 | | | " | 6.68 | -6 | | | |
| | | | | " KBr1 | | | " | 7.63 | -6 | | | |
| | | | | HCl | 4 | | 25 | 8.55 | -6 | | | " |
| | | | | " | " | | 40 | 4.56 | -5 | | | |
| | | | | HCl | 5 | | 25 | 6.02 | -6 | | | |
| | | | | " | " | | 41 | 3.66 | -5 | | | |
| .3 | $CH_3CONH_2 + OH^-$ | $H_2O$ | A = 0.15; B = 0.6 - 1.0 | | | $k$ AB | 18 | 2.0 | -5 | | * | (8) |
| | | | | | | | 25 | 4.0 | -5 | | | |
| | | $H_2O$ | A = 0.05; B = 1 | | | $k$ A | 25 | 4.0 | -5 | | * | (12) |



942151 O—51——17

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $C_2H_5CONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $kA[H^+]$ | 42.1 | 5.9 | -5 | | * | (2) |
| | | | | | | | 63.2 | 4.3 | -4 | | | |
| | | | | | | | 70.3 | 9.2 | -4 | | | |
| | | | | | | | 80.7 | 1.9 | -3 | 19.8 | | |
| | | $H_2O$ | 0.05 - 0.8 | HCl | 1.5 | $kA$ | 25 | 9.40 | -6 | | * | (7) |
| | | | | | 3.0 | | " | 1.39 | -5 | | | |
| | | | | | 3.5 | | " | 1.39 | -5 | | | |
| | | | | | 4.0 | | " | 1.33 | -5 | | | |
| | | | | | 5.0 | | " | 1.17 | -5 | | | |
| | | | | $H_2SO_4$ | 0.093 | " | " | 3.3 | -6 | | | " |
| | | | | | 0.49 | | " | 1.14 | -5 | | | |
| | | | | | 0.825 | | " | 1.47 | -5 | | | |
| | | | | | 1.53 | | " | 1.44 | -5 | | | |
| | | | | | 2.06 | | " | 1.25 | -5 | | | |
| | | | | | 2.65 | | " | 8.9 | -6 | | | |
| | | | | | 3.00 | | " | 7.2 | -6 | | | |
| | | | | | 3.75 | | " | 4.7 | -6 | | | |
| | | | | | 5.60 | | " | 1.7 | -6 | | | |
| | | $H_2O$ | ~ 0.15 | HCl | 1.0 | $kA$ | 18 | 4.6 | -6 | | * | (8) |
| | | | | | | | 25 | 8.3 | -6 | | | |
| | | | " | " | 0.5 | " | 25 | 4.3 | -6 | | | |
| .5 | $C_2H_5CONH_2 + OH^-$ | $H_2O$ | A = 0.15; B = 0.6 - 1.0 | | | $kAB$ | 18 | 2.2 | -5 | | | (8) |
| | | | | | | | 25 | 3.8 | -5 | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $C_3H_7CONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $kA[H^+]$ | 42.1 | 3.0 | -5 | | * | ([2]) |
| | | | | | | | 63.2 | 2.0 | -4 | | | |
| | | | | | | | 70.3 | 4.0 | -4 | | | |
| | | | | | | | 80.7 | 1.0 | -3 | 20.1 | | |
| | | $H_2O$ | ~ 0.15 | HCl | 1.0 | $kA$ | 18 | 2.0 | -6 | | * | ([8]) |
| | | | | | | | 25 | 4.1 | -6 | | | |
| | | | " | " | 0.5 | " | 25 | 2.0 | -6 | | | " |
| .7 | $C_3H_7CONH_2 + OH^-$ | $H_2O$ | A = 0.15; B = 0.6 - 1.0 | | | $kAB$ | 18 | 7.6 | -6 | | * | ([8]) |
| | | | | | | | 25 | 1.5 | -5 | | | |
| .8 | $(CH_3)_2CHCONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $kA[H^+]$ | 42.1 | 3.5 | -5 | | * | ([2]) |
| | | | | | | | 63.2 | 2.5 | -4 | | | |
| | | | | | | | 70.3 | 4.7 | -4 | | | |
| | | | | | | | 80.7 | 1.05 | -3 | 19.5 | | |
| | | $H_2O$ | ~ 0.15 | HCl | 1.0 | $kA$ | 18 | 2.6 | -6 | | * | ([8]) |
| | | | | | | | 25 | 6.0 | -6 | | | |
| .9 | $(CH_3)_2CHCONH_2 + OH^-$ | $H_2O$ | A = 0.15; B = 0.6 - 1.0 | | | $kAB$ | 18 | 7.1 | -6 | | * | ([8]) |
| | | | | | | | 25 | 1.35 | -5 | | | |
| .10 | $C_4H_9CONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $kA[H^+]$ | 63.2 | 5.6 | -5 | | * | ([2]) |
| | | | | | | | 70.3 | 1.0 | -4 | | | |
| | | | | | | | 80.7 | 2.5 | -4 | 20.1 | | |
| | | $H_2O$ | ~ 0.15 | HCl | 1.0 | $kA$ | 18 | 4.0 | -6 | | * | ([8]) |
| | | | | | | | 25 | 8.8 | -6 | | | |
| | | " | " | " | 0.5 | " | 25 | 4.4 | -6 | | | " |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $C_4H_9CONH_2 + OH^-$ | $H_2O$ | A = 0.15; B = 0.6 - 1.0 | | | $kAB$ | 18 | 1.25 | -6 | | | ([8]) |
| | | | | | | | 25 | 2.5 | -6 | | | |
| .12 | $C_5H_{11}CONH_2 + H_2O$ | $H_2O$ | 0.25 - 2.0 | HCl | ~ A | $kA[H^+]$ | 63.2 | 2.0 | -4 | | * | ([2]) |
| | | | | | | | 70.3 | 4.5 | -4 | | | |
| | | | | | | | 80.7 | 1.05 | -3 | | | |
| | | $H_2O$ | ~ 0.15 | HCl | 1.0 | $kA$ | 18 | 2.8 | -6 | | * | ([8]) |
| | | | | | | | 25 | 4.8 | -6 | | | |
| | | | " | " | 0.5 | " | 25 | 1.8 | -6 | | | " |
| .13 | $C_5H_{11}CONH_2 + OH^-$ | $H_2O$ | A = 0.15; B = 0.6 - 1.0 | | | $kAB$ | 18 | 7.1 | -6 | | * | ([8]) |
| | | | | | | | 25 | 1.3 | -5 | | | |
| .14 | $NH_2COCONH_2 + OH^-$ | $H_2O$ | $10^3A = 1 - 3$; $10^3B = 2 - 4$ | | | $kAB$ | 30.1 | 2.3 | -2 | | | ([13]) |
| .15 | $NaOCOCONH_2 + OH^-$ | $H_2O$ | $10^2A = 1 - 5$; $10^2B = 1.4 - 5.5$ | | | $kAB$ | 30.1 | 2.3 | -4 | | | ([13]) |
| .16 | $\underbrace{COCONH} + OH^-$ | $H_2O$ | $10^3A = 1 - 3$; $10^3B = 2 - 5$ | | | $kAB$ | 30.1 | 2.3 | -2 | | | ([13]) |

## COMMENTS

**Literature references:** ([2]) Definition of $k$, not clear from the original, was assumed to be second-order $k\,A[H^+]$. ([5]) The values of $k$ are "means of 5 middle determinations"; actually, $k$ falls with the progress of the reaction, paralleling the fall of the electrometrically measured $[H^+]$ which remains at all stages practically equal to the momentary [A], in accordance with the formulation of the reaction $RCONH_2 + H_2O + H^+ \longrightarrow RCOOH + NH_4^+$. ([8]) Authors erroneously term their $k$ as "bimolecular". Actually it is first-order. For the alkaline hydrolyses with $OH^-$, true second-order constants, as defined in the tables, have been calculated from the original, actually first-order $k$, and found to hold in the given range of variation of $[OH^-]$, 0.6 - 1.0.

**Reactions.** (.2) Fair agreement for first-order $k$ at 25° between ([7]) and ([8]). Plot of the first-order $k$ against the concentration of the acid by ([12]), combining his own data and those of ([8]) at 25° C, and his own data and those of ([4]) and 50° C, shows increase of the first-order $k$ with increasing concentrations of HCl up to about 2.5 - 3.0 M/l, a maximum, and then decrease of $k$ with further increasing concentration of the acid. Order of magnitude of second-order $k$ at 63 - 64° C, $\sim 3.6 \times 10^{-4}$, in fair agreement between ([2]), ([1]), and ([4]). A second-order rate constant defined by $k\,A[H^+]$ at 25° C, $k = 6.0 \times 10^{-6}$, has been averaged from data of ([8]). (.3) Second-order $k$ of ([12]) at 25° C, since given for $[OH^-] = 1$, is in agreement with the first-order $k$ of ([8]). No significant salt effects of 1 *N* NaCl, NaBr, NaI with NaOH, or KCl, KBr, KI with KOH ([12]).

## LITERATURE

([1]) S.F.Acree, S.Nirdlinger, *Am. Chem. J.* 1907, **38**, 489. ([2]) J.C.Crocker, *CSL* 1907, **91**, 593. ([3]) J.C.Crocker, F.H.Lowe, *CSL* 1907, **91**, 952. ([4]) H. v.Euler, A. Olander, *ZPC* 1928, **131**, 107. ([5]) H.v.Euler, E.Rudberg, *ZAC* 1923, **127**, 244. ([6]) S.Kilpi, *ZPC* 1912, **80**, 165. ([7]) V.K.Kreible, K.A.Holst, *ACS* 1938, **60**, 2976. ([8]) N.von Peskoff, J.Meyer, *ZPC* 1913, **82**, 129. ([9]) B.S.Rabinowitch, C.A.Winkler, A.R.P.Stewart, *CJR*[B] 1942, **20**, 121. ([10]) E.E.Reid, *Am. Chem. J.*, 1911, **45**, 327. ([11]) F.E.C.Scheffer, M.J.R.H.van Nouhys, Mme.J.C.Posthumus-Bruyn, *RTC* 1932, **51**, 673. ([12]) T.W.J.Taylor, *CSL* **1930**, 2741. ([13]) F.H.Westheimer, M.W.Shookhoff, *ACS* 1940, **62**, 269.

# SOLVOLYSIS

## C ⋮ N bond solvolysis

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCN + 2H_2O \rightarrow HCOONH_4$ | $H_2O$ | 0.08 - 2.5 | HCl | 0.302 | $k$ A | 65 | 8.06 | -8 | | | | * | (9) (11) |
| | | | | | 1.02 | | " | 5.00 | -7 | | | | | |
| | | | | | 3.17 | | " | 2.64 | -5 | | | | | |
| | | | | | 5.52 | | " | 3.51 | -4 | | | | | |
| | | | " | HBr | 0.30 | " | 65 | 8.06 | -8 | | | | | " |
| | | | | | 4.45 | | " | 1.31 | -5 | | | | | |
| | | | | | 7.13 | | " | 4.56 | -4 | | | | | |
| | | | " | $H_2SO_4$ | 0.508 | | 65 | 1.72 | -7 | | | | | |
| | | | | | 3.82 | | " | 2.99 | -5 | | | | | |
| | | | | | 5.49 | | " | 5.45 | -5 | | | | | |
| | | $H_2O$ | 0.22 | HCl | 8.47 | $k$ A | 0.0 | 2.37 | -6 | | | | * | (12) (13) |
| | | | | | | | 19.8 | 3.50 | -5 | | | | | |
| | | | | | | | 29.7 | 1.09 | -4 | | | | | |
| | | | | | | | 34.7 | 2.05 | -4 | 21.5 | 4.5 | 10 | | |
| | | | 0.44 | " | 1.00 | " | 65 | 5.01 | -7 | | | | | |
| | | | | | | | 80.3 | 2.41 | -6 | | | | | |
| | | | | | | | 99.9 | 1.36 | -5 | 24.7 | 4.5 | 9 | | |
| | | $CH_3COOH$ 95 % | 0.1 - 1.0 | HCl | 0.8 | $k$ A | 0 | 1.15 | -5 | | | | * | (8) |
| | | | | | 1.65 | | " | 2.60 | -4 | | | | | |
| | | | | | 2.65 | | " | 3.48 | -3 | | | | | |
| | | | | | 2.80 | | " | 6.96 | -3 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCN + 2H_2O \rightarrow HCOONH_4$ *(continued)* | $CH_3COOH$ 95 % | 0.1 - 1.0 | HCl | 0.85 | $k$ A | 10 | 6.44 | -5 | | | | | (8) |
| | | | | | 1.65 | | " | 1.07 | -3 | | | | | |
| | | | | | 2.0 | | " | 5.50 | -3 | | | | | |
| | | $CH_3COOH$ 99.97 % | " | " | 1.15 | " | 0 | 1.26 | -4 | | | | | " |
| | | | | | 1.75 | | " | 1.04 | -3 | | | | | |
| | | | | | 2.45 | | " | 6.52 | -3 | | | | | |
| | | " | " | " | 1.0 | " | 10 | 6.20 | -4 | | | | | " |
| | | | | | 1.55 | | " | 3.06 | -3 | | | | | |
| | | | | | 1.85 | | " | 8.65 | -3 | | | | | |
| .2 | $HCN + H_2SO_4 + H_2O \rightarrow CO + NH_4HSO_4$ | $H_2O + H_2SO_4$ (%) | A ~ 0.05 | | | $k$ A | | | | | | | * | (1) |
| | $(HCN \cdot H_2SO_4 + H_2O \rightarrow CO + NH_4HSO_4)$ | 73.1 | | | | | 80 | 9.17 | -5 | | | | | |
| | | 79.0 | | | | | " | 3.95 | -4 | | | | | |
| | | 82.5 | | | | | " | 2.27 | -4 | | | | | |
| | | 64.8 | " | | | " | 90 | 3.34 | -5 | | | | | " |
| | | 79.0 | | | | | " | 8.84 | -4 | 22.3 | | | | |
| | | 91.3 | | | | | " | 8.38 | -5 | 22.9 | | | | |
| | | 64.8 | " | | | " | 100 | 1.18 | -4 | 33.3 | | | | " |
| | | 78.1 | | | | | " | 2.37 | -3 | | | | | |
| | | 95.9 | | | | | " | 5.33 | -5 | 23.5 | | | | |
| .2.1 | $HCN + H_2SO_4 \rightarrow HCN \cdot H_2SO_4$ | $H_2SO_4$ 100 % | B/A = 1 | | | $k$ | 0 | 5.66 | -4 | | | | * | (1) |
| | | | | | | | 10 | 2.00 | -3 | 18.6 | | | | |
| | | 96.2 % | " | | | " | 0 | 9.02 | -5 | | | | | " |
| | | | | | | | 10 | 3.50 | -4 | 20.8 | | | | |
| | | $H_2SO_4$ 100 % | B/A ⩾ 7 | | | $k$ A | 0 | 1.64 | -4 | | | | | " |
| | | | | | | | 10 | 3.10 | -4 | 15.9 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .2.1 | $HCN + H_2SO_4 \rightarrow HCN \cdot H_2SO_4$ *(continued)* | 96.2 % | B/A ⩾ 7 | | | $k$ A | 0 | 5.13 | -5 | | | | | |
| | | | | | | | 10 | 1.86 | -4 | 19.5 | | | | |
| .3 | $HCN + H_3PO_4 + H_2O \rightarrow CO + NH_4H_2PO_4$ | $H_2O + H_3PO_4$ (%) | A ~ 0.05 | | | $k$ A | | | | | | | | |
| | | 100 | | | | | 100 | 1.44 | -4 | | | | * | (1) |
| | $(HCN \cdot H_3PO_4 + H_2O \rightarrow CO + NH_4H_2PO_4$ | 100 | | | | | 110 | 3.44 | -4 | | | | | " |
| | | 93.3 | | | | | " | 9.25 | -5 | | | | | |
| | | 88.0 | | | | | " | 3.45 | -5 | | | | | |
| | | 100 | | | | | 120 | 7.38 | -4 | | | | | " |
| | | 93.3 | | | | | " | 2.24 | -4 | | | | | |
| | | 88.0 | | | | | " | 8.87 | -5 | | | | | |
| | | 100 | | | | | 130 | 1.60 | -3 | 23.5 | | | | " |
| | | 93.3 | | | | | " | 5.32 | -4 | | | | | |
| | | 88.0 | | | | | " | 2.10 | -4 | | | | | |
| | | 93.3 | | | | | 140 | 1.05 | -3 | 25.8 | | | | " |
| | | 88.0 | | | | | " | 4.55 | -4 | 26.9 | | | | |
| .4 | $NH_2CN + H_2O \rightarrow (NH_2)_2CO$ | $H_2O$ | 0.5 | $H_2SO_4$ | 0.06 | $k$ A | 50 | 3.1 | -5 | | | | * | (5) |
| | | $H_2O$ | 0.25 | $H_2SO_4$ | 0.036 | $k$ A | 50.4 | 1.63 | -5 | | | | * | (2) |
| | | | | | 0.0675 | | " | 3.13 | -5 | | | | | |
| | | | | | 0.135 | | " | 6.21 | -5 | | | | | |
| | | | | | 0.494 | | " | 2.48 | -4 | | | | | |
| | | | " | $HNO_3$ | 0.059 | " | 50.4 | 2.14 | -5 | | | | | " |
| | | | | | 0.118 | | " | 4.15 | -5 | | | | | |
| | | | | | 0.237 | | " | 8.35 | -5 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $NH_2CN + H_2O \rightarrow (NH_2)_2CO$ *(continued)* | | 0.23 | $HNO_3$ + $CO(NH_2)_2$ | 0.249 | | | | | | | | | |
| | | | | | 1.0 | $kA$ | 50.4 | 4.22 | -5 | | | | | (2) |
| | | | 0.25 | $HNO_3$ | 0.126 | " | 25.0 | 3.41 | -6 | | | | | " |
| | | | | | 0.252 | | " | 6.88 | -6 | | | | | |
| | | | | | 0.526 | | " | 2.00 | -5 | | | | | |
| | | | | | 1.05 | | " | 3.48 | -5 | | | | | |
| | | | | | 2.14 | | " | 9.62 | -5 | | | | | |
| | | | | | 4.26 | | " | 3.71 | -4 | | | | | |
| | | $H_2O$ | 0.21 - 0.25 | $HNO_3$ | 0.5947 | $kA$ | 25.0 | 1.99 | -5 | | | | * | (15) (7) |
| | | | | | 1.490 | | " | 6.27 | -5 | | | | | |
| | | | | | 2.512 | | " | 1.49 | -4 | | | | | |
| | | | | | 3.881 | | " | 3.70 | -4 | | | | | |
| | | | " | " | 0.9944 | " | 30.0 | 6.27 | -5 | | | | | " |
| | | | | | 1.490 | | " | 1.09 | -4 | | | | | |
| | | | | | 2.512 | | " | 2.56 | -4 | 19.3 | | | | |
| | | | | | 3.881 | | " | 6.28 | -4 | | | | | |
| | | $H_2O$ | 0.036 | $HClO_4$ | 0.4844 | $kA$ | 30.0 | 2.48 | -5 | | | | | " |
| | | $H_2O$ | 0.045 | HCl | 0.2474 | $kA$ | 25.0 | 7.37 | -6 | | | | * | " |
| | | | | | 0.9820 | | " | 3.33 | -5 | | | | | |
| | | | | | 1.613 | | " | 4.93 | -5 | | | | | |
| | | | | | 2.066 | | " | 4.48 | -5 | | | | | |
| | | | | | 2.935 | | " | 1.81 | -5 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $NH_2CN + H_2O \rightarrow (NH_2)_2CO$ *(continued)* | | 0.045 | HCl | 0.0959 | *k* A | 30.0 | 4.73 | -6 | | | | | (15) (7) |
| | | | | | 0.2474 | | " | 1.28 | -5 | 19.9 | | | | |
| | | | | | 0.9820 | | " | 5.68 | -5 | | | | | |
| | | | | | 1.613 | | " | 8.63 | -5 | | | | | |
| | | | | | 2.066 | | " | 7.89 | -5 | 20.3 | | | | |
| | | | | | 2.935 | | " | 3.34 | -5 | 22.0 | | | | |
| | | $H_2O$ | 0.25 | NaCl + HCl = 4.0 | | *k* A | | | | | | | | |
| | | | | HCl | 0.500 | | 30.0 | 3.51 | -5 | | | | * | (15) (7) |
| | | | | | 1.000 | | " | 4.46 | -5 | | | | | |
| | | | | | 2.000 | | " | 3.21 | -5 | | | | | |
| | | | | | 4.000 | | " | 9.03 | -6 | | | | | |
| | | | | | 0.500 | " | 40.0 | 1.01 | -4 | | | | | " |
| | | | | | 1.000 | | " | 1.10 | -4 | | | | | |
| | | | | | 2.000 | | " | 9.83 | -5 | | | | | |
| | | | | | 4.000 | | " | 3.14 | -5 | | | | | |
| | | $H_2O$ | 0.21 - 0.25 | HBr | 1.010 | *k* A | 25.0 | 3.36 | -5 | | | | * | (15) (7) |
| | | | | | 1.499 | | " | 5.55 | -5 | | | | | |
| | | | | | 2.097 | | " | 9.00 | -5 | | | | | |
| | | | | | 2.534 | | | 1.16 | -4 | | | | | |
| | | | " | " | 0.7492 | " | 30.0 | 3.98 | -5 | | | | * | " |
| | | | | | 1.010 | | " | 5.63 | -5 | 18.4 | | | | |
| | | | | | 1.499 | | " | 9.28 | -5 | 19.0 | | | | |
| | | | | | 2.097 | | " | 1.54 | -4 | 19.4 | | | | |
| | | | | | 2.534 | | " | 2.01 | -4 | 19.6 | | | | |
| | | | | | 2.642 | | " | 2.09 | -4 | | | | | |
| | | | | | 3.038 | | " | 2.47 | -4 | | | | | |
| | | | | | 4.027 | | " | 1.89 | -4 | | | | | |
| | | | | | 5.178 | | " | 3.95 | -5 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $NH_2CN + H_2O \rightarrow (NH_2)_2CO$ *(continued)* | | 0.21 - 0.25 | HBr | 0.7492 | $k$ A | 40.0 | 1.07 | -4 | 18.4 | | | * | (15) (7) |
| | | | | | 2.642 | | " | 5.85 | -4 | 19.4 | | | | |
| | | | | | 3.038 | | " | 6.88 | -4 | 19.4 | | | | |
| | | | | | 4.027 | | " | 5.68 | -4 | 20.6 | | | | |
| | | | | | 5.178 | | " | 1.36 | -4 | 23.3 | | | | |
| | | $H_2O$ | 0.19 - 0.25 | $CCl_3COOH$ | 0.2497 | $k$ A | 25.0 | 1.62 | -5 | | | | * | " |
| | | | | | 1.022 | | " | 9.48 | -5 | | | | | |
| | | | | | 2.040 | | " | 2.34 | -4 | | | | | |
| | | | | | 2.905 | | " | 3.39 | -4 | | | | | |
| | | | | | 3.971 | | " | 4.33 | -4 | | | | | |
| .5 | $CH_3CN + 2H_2O \rightarrow CH_3COONH_4$ | $H_2O$ | ~ 0.22 | HCl | 0.51 | $k$ A | 59.6 | 3.65 | -8 | | | | | (12) (13) |
| | | | " | " | 1.00 | " | 59.6 | 8.03 | -8 | | | | | |
| | | | | | | | 83.5 | 1.20 | -6 | | | | | |
| | | | | | | | 93.3 | 3.23 | -6 | | | | | |
| | | | | | | | 99.7 | 6.32 | -6 | | | | | |
| | | | | | | | 111.8 | 1.84 | -5 | 26.5 | 2.1 | 10 | | |
| | | | | " | 2.00 | " | 59.6 | 2.13 | -7 | | | | | |
| | | | | " | 4.00 | " | 49.6 | 2.78 | -7 | | | | | |
| | | | | | | | 59.6 | 9.10 | -7 | | | | | |
| | | | | | | | 80.6 | 9.36 | -6 | | | | | |
| | | | | | | | 94.1 | 3.82 | -5 | | | | | |
| | | | | | | | 99.5 | 6.33 | -5 | 25.8 | 2.0 | 10 | | |
| | | | " | " | 5.00 | " | 59.6 | 2.66 | -6 | | | | | " |
| | | | | | | | 70.1 | 8.49 | -6 | | | | | |
| | | | | | | | 83.1 | 2.98 | -5 | | | | | |
| | | | | | | | 99.7 | 1.37 | -4 | 24.2 | 4.0 | 9 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $CH_3CN + 2H_2O \rightarrow CH_2COONH_4$ *(continued)* | | ~ 0.22 | HCl | 8.47 | $kA$ | 28.4 | 5.77 | -6 | | | | | (12) (13) |
| | | | | | | | 42.7 | 2.74 | -5 | | | | | |
| | | | | | | | 49.6 | 5.68 | -5 | | | | | |
| | | | | | | | 59.6 | 1.52 | -4 | 21.0 | 1.3 | 9 | | |
| .6 | $CH_3CN + H_2O \rightarrow CH_3CONH_2$ | $H_2O$ | | HCl | 2 | $kA$ | 65 | 1.66 | -7 | | | | | (10) |
| | | | | | 4 | | " | 5.65 | -7 | | | | | |
| | | | | | 6 | | " | 2.16 | -6 | | | | | |
| | | | | | 8 | | " | 1.07 | -5 | | | | | |
| | | | | | 10 | | " | 2.99 | -5 | | | | | |
| | | | | $H_2SO_4$ | 2 | " | 65 | 2.36 | -7 | | | | | " |
| | | | | | 4 | | " | 7.36 | -7 | | | | | |
| | | | | | 6 | | " | 1.68 | -6 | | | | | |
| | | | | | 8 | | " | 2.95 | -6 | | | | | |
| .7 | $C_2H_5CN + 2H_2O \rightarrow C_2H_5COONH_4$ | $H_2O$ | 0.20 | HCl | 0.51 | $kA$ | 59.6 | 7.2 | -8 | 25.6 | 1.1 | 10 | * | (13) |
| | | | " | " | 2.00 | " | 59.6 | 4.2 | -7 | | | | | |
| | | " | 0.40 | HBr | 1.00 | " | 86.7 | 2.84 | -6 | | | | * | (14) |
| | | | | | | | 124.8 | 8.55 | -5 | 25.7 | 1.1 | 10 | | |
| | | " | 0.40 | $H_2SO_4$ | 1.00 | " | 86.5 | 3.20 | -6 | | | | * | " |
| | | | | | | | 113.6 | 3.94 | -5 | | | | | |
| | | | | | | | 125.3 | 1.05 | -4 | | 1 | 10 | | |
| | | " | 0.40 | $HNO_3$ | 1.00 | " | 80.5 | 2.60 | -6 | | | | * | " |
| | | | | | | | 124.8 | 9.20 | -5 | 26.5 | 5 | 10 | | |
| | | " | " | " | 4.00 | " | 78.7 | 1.29 | -5 | | | | | " |
| | | | | | | | 107.4 | 2.05 | -4 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $C_2H_5CN + H_2O \rightarrow C_2H_5CONH_2$ | $H_2O$ | | HCl | 4 | $kA$ | 65 | 1.00 | -6 | | | | | ([10]) |
| | | | | | 6 | | " | 4.00 | -6 | | | | | |
| | | | | | 8 | | " | 2.17 | -5 | | | | | |
| | | | | | 14.9 | | " | 3.90 | -5 | | | | | |
| | | " | | $H_2SO_4$ | 4 | | | | | | | | | |
| | | | | | 6 | " | 65 | 1.28 | -6 | | | | | |
| | | | | | | | " | 2.52 | -6 | | | | | |
| .9 | $C_2H_5CN + \begin{cases} H_2O \\ 2H_2O \end{cases} \rightarrow \begin{cases} C_2H_5CONH_2 & (a) \\ C_2H_5COONH_4 & (b) \end{cases}$ | $H_2O$ | | | $(a + b) = kA$ | | | | | | | | | |
| | | | 0.1995 | HCl | 6.48 | | 3.83 | 2.76 | -6 | | | | * | ([13]) |
| | | | | | | | 49.9 | 9.75 | -6 | | | | | |
| | | | | | | | 59.6 | 2.78 | -5 | | | | | |
| | | | | | | | 72.6 | 9.00 | -5 | 21.8 | 8 | 8 | | |
| | | " | 0.1770 | " | 10.13 | " | 0.0 | 4.8 | -6 | | | | | " |
| | | | | | | | 16.8 | 3.36 | -5 | | | | | |
| | | | | | | | 24.7 | 8.45 | -5 | | | | | |
| | | | | | | | 34.5 | 2.21 | -4 | 18.9 | 6 | 8 | | |
| | | " | 0.1638 | HBr | 7.68 | " | 48.7 | 1.01 | -5 | | | | * | ([14]) |
| | | | | | | | 79.7 | 2.22 | -4 | 22.6 | 3.5 | 5 | | |
| | | " | 0.5244 | $H_2SO_4$ | 5.30 | " | 58.5 | 5.75 | -6 | | | | * | " |
| | | | | | | | 80.6 | 5.74 | -5 | 24.4 | 1.1 | 10 | | |
| | | " | 0.3883 | " | 9.43 | " | 48.7 | 3.42 | -5 | | | | * | " |
| | | | | | | | 68.1 | 1.88 | -4 | 23.0 | 3.0 | 10 | | |
| | | " | 0.2593 | $HNO_3$ | 13.01 | " | 48.7 | 1.36 | -5 | | | | * | " |
| | | | | | | | 68.1 | 8.30 | -5 | | | | | |
| | | | | | | | 80.5 | 2.50 | -4 | 20.7 | 1.3 | 9 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .10 | $CH_2OHCH_2CN + H_2O \rightarrow CH_2OHCH_2CONH_2$ | $H_2O$ | | HCl | 4 | $kA$ | 65 | 5.15 | -7 | | | | | (10) |
| | | | | | 6 | | " | 1.83 | -6 | | | | | |
| | | | | | 8 | | " | 9.64 | -6 | | | | | |
| | | | | $H_2SO_4$ | 4 | " | 65 | 7.5 | -7 | | | | | " |
| | | | | | 6 | | " | 1.75 | -6 | | | | | |
| .11 | $CH_3CHOHCN + H_2O \rightarrow CH_3CHOHCONH_2$ | $H_2O$ | | HCl | 4 | $kA$ | 65 | 7.77 | -6 | | | | | (10) |
| | | | | | 6 | | " | 7.[illegible] | -5 | | | | | |
| | | | | | 8 | | " | 2.80 | -4 | | | | | |
| | | | | $H_2SO_4$ | 4 | " | 65 | 1.69 | -6 | | | | | " |
| | | | | | 6 | | " | 4.86 | -6 | | | | | |
| .12 | $COOHCH_2CN + 2H_2O \rightarrow COOHCH_2COONH_4$ | $H_2O$ | 0.185 | HCl | 1.00 | $kA$ | 99.5 | 2.81 | -6 | | | | | (12) (13) |
| | | | | | | | 110.2 | 7.40 | -6 | | | | | |
| | | | | | | | 125.4 | 2.82 | -5 | 26.3 | 7.9 | 9 | | |
| | | | " | " | 4.00 | " | 59.6 | 6.23 | -7 | | | | | " |
| | | | | | | | 90.5 | 1.57 | -5 | | | | | |
| | | | | | | | 99.5 | 3.75 | -5 | | | | | |
| | | | | | | | 109.9 | 1.02 | -4 | 25.5 | 7.9 | 9 | | |
| .13 | $COOHCH_2CN + H_2O \rightarrow COOHCH_2CONH_2$ | $H_2O$ | | HCl | 2 | $kA$ | 65 | 7.80 | -8 | | | | | (10) |
| | | | | | 4 | | " | 3.34 | -7 | | | | | |
| | | | | | 6 | | " | 2.30 | -6 | | | | | |
| | | | | | 8 | | " | 1.72 | -5 | | | | | |
| | | " | | $H_2SO_4$ | 4 | " | 65 | 3.5 | -7 | | | | | " |
| | | | | | 6 | | " | 7.4 | -7 | | | | | |
| | | | | | 8 | | " | 1.57 | -6 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .14 | $2,7-C_{10}H_6(CN)_2 + OH^- + H_2O \rightarrow 2,7-C_{10}H_6(CN)COO^- + NH_3$ | $C_5H_{11}OH$ | A = 0.0056 - 0.013<br>B = 0.011 - 0.016 | | | $kA$ | 121 - 126 | ~ 2.5 | -4 | | | | * | (6) |
| .15 | $2,7-C_{10}H_6(CN)COO^- + OH^- + H_2O \rightarrow 2,7-C_{10}H_6(COO^-)_2 + NH_3$ | $C_5H_{11}OH$ | " | | | " | 121 - 126 | 3.5<br>~ 4.2 | -5<br>-5 | | | | * | (6) |

942151 O—51——18

## COMMENTS

(.1) Data of ([9]) ([12]) at 65° C in HCl 1M/l, $k = 5.0 \times 10^{-7}$ (underlined in table), in excellent agreement with ([12]) ([13]). In $CH_3COOH$, hydrolysis is about $10^6$ times faster than in $H_2O$ under the same conditions ([8]). Further data in different $CH_3COOH + H_2O$ solutions, and with $(CH_3CO)_2O$ added, in original ([8]). Rates clearly increase very much faster than proportionally to the acid concentration. Mechanism discussion, see ([7]). (.2) (.2.1) In concentrated $H_2SO_4$, the rate is strictly first-order in HCN in the presence of a large excess of $H_2SO_4$, but becomes more nearly of the zero order when the concentration of HCN becomes comparable to that of $H_2SO_4$. Convincing evidence is given ([1]) for a mechanism involving reaction (.2.1) as a first step of the overall reaction (.2). The compound $HCN \cdot H_2SO_4$ was actually isolated, and this justifies the alternative formulation of reaction (.2) written in the table in parentheses. $HCN \cdot H_2SO_4$ is assumed to react further according to $HCN \cdot H_2SO_4 + H_2O \rightleftarrows HCONH_2 \cdot H_2SO_4$ (this intermediate not actually isolated) $\rightarrow CO + NH_4HSO_4$. Evidence for this mechanism is the observation that, in $H_2SO_4$ of the same high concentration, the half-lives of HCN and of $HCONH_2$ are very exactly equal. Reaction (.2.1), the rate-determining step of (.2), is zero-order $k$ at comparable concentrations of HCN and $H_2SO_4$, first-order ($k$ A) in the presence of a large excess of $H_2SO_4$. The zero-order rate given in the table was recalculated to M/l per sec from the original M/ml per min; the first-order $k$ was calculated from the original half-lives ([1]). For the overall reaction (.2), note the maxima of $k$ at 78 - 79 % $H_2SO_4$; on each side of the maximum, $\Delta \log k/\Delta(\%\ H_2SO_4)$ is constant. In $H_2SO_4 > 90$ %, some $SO_2$ and $CO_2$ is formed in addition to CO. Data at further temperatures in original ([1]). (.3) Same mechanism and same considerations as for (.2) (.2.1). The compound $HCN \cdot H_3PO_4$ was isolated. The system is two-phase; the reaction takes place in the $H_3PO_4$ phase. For the rate-determining step $HCN + H_3PO_4$ in 100 % $H_3PO_4$ is 3.6 days. In the same concentrated $H_3PO_4$, the half-lives of HCN and of $HCONH_2$ are equal, which bears out the assumed intermediate $HCONH_2 \cdot H_3PO_4$. (.4) Selected points. The $k$ data of ([2]) had to be multiplied by 2.3 (conversion from $\log_{10}$ to ln) to fall in line with the figure of ([5]), and to check with ([15]). Proportionality of $k$ with the acid concentration is approximately fulfilled only at very low acid concentrations; in stronger acid, $k$ increases much faster than linearly with the acid concentration ([2]). This increase is represented by ([3]) as exponential, the rate $v = v_o e^{kc}$, where $v_o$ is the rate at zero concentration $c$ of the acid; for $HNO_3$ at 25° C, $k = 0.265$ in the $HNO_3$ concentration range 0.05 - 5.0. ([3]). Values of

## COMMENTS *(continued)*

$k$ are given also for salts ($KNO_3$, $NH_4NO_3$, $NaNO_3$, $LiNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$) at constant $[HNO_3]$. In $HNO_3$, the activation energy $E$ is independent of $[HNO_3]$ in the range 0.12 - 1.98, but it varies in HCl ([7])([15]). With increasing concentration of HCl or HBr, $k$ increases to a maximum, then falls off ([7]). In $[HCl] + [NaCl]$ = constant = 4.0, $\log (k/[HCl])$ is a linear function of $[HCl]$ ([7]). In $CCl_3COOH$, the plot of $k$ against $[CCl_3COOH]$ approaches a straight line passing through the origin ([7]). Further data of $k$ in dilute acids and in buffer solutions, see original ([7]). The mechanism is represented by $NH_2CN + H^+ \rightarrow NH_2CN \cdot H^+$, followed by $NH_2CN \cdot H^+ + H_2O \rightarrow NH_2CN \cdot H_3O^+$; subsequent reactions, and mechanism discussions, see in particular ([15]), and ([4]). **(.5) (.6) (.7) (.8) (.9)** Selected points. Salt effects present. **(.14) (.15)** From overall rate of two-step reaction.

## LITERATURE

(1) A.W.Cobb, J.H.Walton, *JPC* 1927, **41**, 351. (2) G.Grube, G.Motz, *ZPC* 1925, **118**, 145.

(3) G.Grube, G.Schmidt, *ZPC* 1926, **119**, 19. (4) Hammett and Paul, *ACS* 1934, **56**, 830.

(5) H.C.Hetherington, J.M.Braham, *ACS* 1923, **45**, 824. (6) F.Kaufler, *ZPC* 1906, **55**, 502.

(7) Mary L.Kilpatrick, *ACS* 1947, **69**, 40. (8) V.K.Krieble, F.C.Duennebier, E.Colton, *ACS* 1943, **65**, 1479. (9) V.K. Krieble, J. G. McNally, *ACS* 1929, **51**, 3368.

(10) V.K.Krieble, C.I.Noll, *ACS* 1939, **61**, 560.

(11) V.K.Krieble, A.L.Peiker, *ACS* 1933, **55**, 2326. (12) B.S.Rabinovitch, C.A.Winkler, *CJR*[B] 1942, **20**, 221. (13) B.S.Rabinovitch, C.A.Winkler, A.R.P.Stewart, *CJR*[B] **20**, 121. (14) B. S. Rabinovitch, C. A. Winkler, A. R. P. Stewart, *CJR*[B] **20**, 168.

(15) M.J.Sullivan, M.L.Kilpatrick, *ACS* 1945, **67**, 1815.

# SOLVOLYSIS

## $N_2$:C bond Solvolysis

*Liquid phase*

Reaction type $N_2CHCOOR' + ROH \rightarrow N_2 + ROCH_2COOR'$

Rate measured $+ d[N_2] / dt$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $N_2CHCOOC_2H_5 + H_2O \rightarrow$ | $H_2O$ | $10^2A =$ | $HNO_3$; $10^4 [H^+] =$ | $k A [H^+]$ | | | | | | | * | (10) |
| | | | 3.76 | 53.67 | | 0.1 | 4.08 | -2 | | | | | |
| | | | 3.09 | 107.4 | | " | 4.36 | -2 | | | | | |
| | | | 1.31 | 286.5 | | " | 4.45 | -2 | | | | | |
| | | | 3.94 | 17.90 | | 5.0 | 7.24 | -2 | | | | | |
| | | | 1.67 | 107.4 | | " | 7.85 | -2 | | | | | |
| | | | 0.95 | 214.9 | | " | 7.75 | -2 | | | | | |
| | | | 3.22 | 26.85 | | 10.0 | 1.25 | -1 | | | | | |
| | | | 2.24 | 107.4 | | " | 1.29 | -1 | | | | | |
| | | | 1.38 | 286.5 | | " | 1.39 | -1 | | | | | |
| | | | 3.62 | 26.83 | | 14.9 | 2.17 | -1 | | | | | |
| | | | 1.28 | 107.3 | | " | 2.27 | -1 | | | | | |
| | | | 1.50 - 3.26 | 26.80 | | 20.3 | 3.82 | -1 | | | | | |
| | | | 1.90 | 107.2 | | " | 3.91 | -1 | | | | | |
| | | | 2.80 - 3.84 | 13.40 | | 25.0 | 5.99 | -1 | | | | | |
| | | | 1.93 | 35.70 | | " | 6.36 | -1 | | | | | |
| | | | 0.67 - 3.36 | 71.39 | | " | 6.22 | -1 | | | | | |
| | | | 1.19 - 1.49 | 107.1 | | " | 6.42 | -1 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $N_2CHCOOC_2H_5 + H_2O$ (*continued*) | | 3.48 | | 5.350 | | 30.0 | 6.78 | -1 | | | | | |
| | | | 1.76 | | 53.50 | | " | 1.02 | 0 | | | | | |
| | | | 4.36 | | 5.342 | | 35.2 | 1.25 | 0 | | | | | |
| | | | 2.04 | | 26.69 | | " | 1.58 | 0 | | | | | |
| | | | 2.72 | | 5.325 | | 40.1 | 1.92 | 0 | | | | | |
| | | | 1.92 | | 13.36 | | " | 2.30 | 0 | | | | | |
| | | | 1.91 | | 26.65 | | " | 2.62 | 0 | | | | | |
| | | | 2.60 | | 1.329 | | 45.1 | 1.55 | 0 | | | | | |
| | | | 3.11 | | 5.318 | | " | 2.83 | | | | | | |
| | | | 1.68 | | 8.888 | | " | 3.53 | 0 | | | | | |
| | | | 1.53 | | 1.323 | | 55.1 | 4.45 | 0 | | | | | |
| | | | 1.17 | | 3.529 | | " | 5.69 | 0 | | | | | |
| | | | 1.07 | | 7.057 | | " | 7.06 | 0 | | | | | |
| | | | 1.69 | | 2.634 | | 65.1 | 1.01 | +1 | | | | | |
| | | | 0.78 | | 5.267 | | " | 1.26 | +1 | 17.5 | 4.27 | 12 | | |
| | | $H_2O$ | | X = | $10^3X$ = | $kA[H^+]$ | 25.0 | | | | | | * | (7) |
| | | | | o-$NH_2C_6H_4COOH$ | 2 - 16 | | " | | | | | | | |
| | | | | p-$NH_2C_6H_4COOH$ | 5 - 16 | | " | | | | | | | |
| | | | | m-$NH_2C_6H_4COOH$ | 5 - 16 | | " | 6.42 | -1 | | | | | |
| | | | | d-$COOHCH(NH_2)CH_2COOH$ | 2 - 4 | | " | | | | | | | |
| | | | | d-$COOHCH(NH_2)CH_2CH_2COOH$ | 2 - 4 | | " | | | | | | | |
| .1.1 | $N_2CHCOOC_2H_5 + H_2O$ | $H_2O + D_2O(N)$ | 0 | | | $kA$ | 15 | 2.37 | -1 | | | | * | (5) |
| | | | 0.204 | | | | " | 3.19 | -1 | | | | | |
| | | | 0.447 | | | | " | 3.97 | -1 | | | | | |
| | | | 0.585 | | | | " | 4.71 | -1 | | | | | |
| | | | 0.843 | | | | " | 6.08 | -1 | | | | | |
| | | | 1.00 | | | | " | 7.48 | -1 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1.1 | $N_2CHCOOC_2H_5 + H_2O$ (*continued*) | $H_2O$ | | | | $k$ A | 0 | 4.17 | -2 | | | | | |
| | | | | | | | 15 | 2.37 | -1 | | | | | |
| | | | | | | | 25 | 6.50 | -1 | | | | | |
| | | | | | | | 35 | 1.67 | 0 | 17.8 | | | | |
| | | $D_2O$ (98 - 99 %) | | | | | 0 | 1.38 | -1 | | | | | |
| | | | | | | | 15 | 7.18 | -1 | | | | | |
| | | | | | | | 25 | 1.80 | 0 | | | | | |
| | | | | | | | 35 | 5.00 | 0 | 17.0 | | | | |
| .2 | $N_2CHCOOCH_3 + C_2H_5OH$ | $B + H_2O$ ($M$/l) | 0.0 | $CCl_3COOH$ | 0.0909 | $k$ A | 25 | 2.40 | -4 | | | | * | ([1]) |
| | | | 0.152 | | " | | " | 1.19 | -4 | | | | | |
| | | | 0.352 | | " | | " | 7.10 | -5 | | | | | |
| | | | 0.0 | $(NO_2)_3C_6H_2OH$ | 0.00227 | " | " | 2.92 | -4 | | | | | |
| | | | 0.069 | | " | | " | 2.15 | -4 | | | | | " |
| | | | 0.0 | " | 0.00455 | " | " | 4.74 | -4 | | | | | |
| | | | 0.106 | | " | | " | 2.89 | -4 | | | | | " |
| | | | 0.344 | | " | | " | 1.32 | -4 | | | | | |
| | | | 0.0 | | 0.00909 | " | " | 7.80 | -4 | | | | | |
| | | | 0.0975 | | " | | " | 4.63 | -4 | | | | | " |
| | | | 0.344 | | " | | " | 2.15 | -4 | | | | | |
| .3 | $N_2CHCOOC_2H_5 + CH_3OH$ | | 0.08 - 0.55 | $(NO_2)_3C_6H_2COOH$ | | $k$ A | | | | | | | * | ([8]) |
| | | $B + H_2O$ ($M$/l) | 0.0 | | 0.00909 | | 25 | 6.12 | -3 | | | | | |
| | | | 0.64 | | " | | " | 3.12 | -3 | | | | | |
| | | | 1.91 | | " | | " | 1.49 | -3 | | | | | |
| | | | 0.0 | " | 0.00455 | " | " | 3.60 | -3 | | | | | |
| | | | 0.32 | | " | | " | 2.24 | -3 | | | | | " |
| | | | 1.28 | | " | | " | 1.08 | -3 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $N_2CHCOOC_2H_5 + CH_3OH$ (*continued*) | | 0.0 | $(NO_2)_3C_6H_2COOH$ | 0.00227 | $kA$ | 25 | 2.05 | -3 | | | | | ([8]) |
| | | | 0.32 | " | " | " | 1.19 | -3 | | | | | | |
| | | | 1.28 | | " | " | 5.58 | -4 | | | | | | |
| .4 | $N_2CHCOOC_2H_5 + C_2H_5OH$ | | 0.08 - 0.55 | $(NO_2)_3C_6H_2COOH$ | | $kA$ | | | | | | | | |
| | | $B + H_2O$ ($M$/l) | 0.0 | | 0.00909 | | 25 | 9.50 | -4 | | | | * | ([8]) |
| | | | 0.32 | | " | | " | 4.26 | -4 | | | | | |
| | | | 2.56 | | " | | " | 1.07 | -4 | | | | | |
| | | | 5.12 | | " | | " | 7.25 | -5 | | | | | |
| | | | 10.2 | | " | | " | 8.16 | -5 | | | | | |
| | | | 15 | | " | | " | 1.16 | -4 | | | | | |
| | | | 0.0 | " | 0.00455 | " | " | 5.72 | -4 | | | | | " |
| | | | 0.16 | | " | | " | 3.54 | -4 | | | | | |
| | | | 0.64 | | " | | " | 1.56 | -4 | | | | | |
| | | | 0.0 | " | 0.00114 | " | " | 1.83 | -4 | | | | | " |
| | | | 0.08 | | " | | " | 1.28 | -4 | | | | | |
| | | $B + H_2O$ ($M$/l) | 0.0 | $CCl_3COOH$ | 0.0445 | $kA$ | 25 | 1.92 | -4 | | | | * | ([1]) |
| | | | 0.0445 | | " | | " | 1.45 | -4 | | | | | |
| | | | 0.149 | | " | | " | 1.00 | -4 | | | | | |
| | | | 0.288 | | " | | " | 6.88 | -5 | | | | | |
| | | | 0.0 | " | 0.182 | " | " | 4.62 | -4 | | | | | " |
| | | | 0.0427 | | " | | " | 3.74 | -4 | | | | | |
| | | | 0.205 | | " | | " | 2.04 | -4 | | | | | |
| | | | 0.336 | | " | | " | 1.51 | -4 | | | | | |
| | | | 0.0 | $(NO_2)_3C_6H_2COOH$ | 0.0445 | " | " | 1.10 | -4 | | | | | " |
| | | | 0.33 | | " | | " | 3.67 | -5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $N_2CHCOOC_2H_5 + C_2H_5OH$ (*continued*) | | 0.0 | $(NO_2)_3C_6H_2COOH$ | 0.182 | | 25 | 4.62 | -4 | | | | | (1) |
| | | | 0.107 | | " | | " | 2.73 | -4 | | | | | |
| | | | 0.336 | | " | | " | 1.46 | -4 | | | | | |
| | | | 0.0 | $HSO_3C_6H_3(OH)COOH$ | 0.00182 | $kA$ | " | 1.18 | -3 | | | | | (1) |
| | | | 0.103 | | | | " | 7.13 | -4 | | | | | |
| | | | 0.426 | | | | " | 2.86 | -4 | | | | | |
| .5 | $N_2CHCOOC_2H_5 + (CH_3)_2CHCH_2OH$ | | 0.08 - 0.55 | $(NO_2)_3C_6H_2COOH$ | | $kA$ | | | | | | | | |
| | | $B + H_2O$ ($M/l$) | 0.0 | | 0.00909 | | 25 | 1.62 | -4 | | | | * | (8) |
| | | | 0.32 | | " | | " | 4.50 | -5 | | | | | |
| .6 | $N_2CHCOOC_2H_5 + CH_2ClCOOH$ | $C_6H_6$ | $10^3A = 7.5 - 11$ | | | $kA$ | 15 | | | | | | | |
| | | | $10^2B = 6 - 64$ | | $k = aB^2 + bB$ | | $a$ | 2.00 | -4 | | | | * | (2) |
| | | | | | | | $b$ | 7.50 | -6 | | | | | |
| | | $C_6H_5CH_3$ | B = 0.25 | | | $kA$ | 25.0 | | | | | | | |
| | | | - 0.80 | | $k = aB^2 + bB$ | | $a$ | 2.24 | -4 | | | | * | (6) |
| | | | | | | | $b$ | 3.10 | -5 | | | | | |
| | | $C_6H_5NO_2$ | 0.15 - 1.2 | | | " | $a$ | 1.10 | -3 | | | | | " |
| | | | | | | | $b$ | 7.50 | -4 | | | | | |
| | | $o$-$CH_3C_6H_4NO_2$ | 0.26 - 0.83 | | | " | $a$ | 1.50 | -3 | | | | | " |
| | | | | | | | $b$ | 1.67 | -4 | | | | | |
| | | $m$-$CH_3C_6H_4NO_2$ | 0.15 - 0.97 | | | " | $a$ | 8.33 | -4 | | | | | " |
| | | | | | | | $b$ | 5.00 | -4 | | | | | |
| | | $C_6H_5Cl$ | 0.22 - 0.69 | | | " | $a$ | 7.48 | -4 | | | | | " |
| | | | | | | | $b$ | 8.80 | -5 | | | | | |
| | | $C_6H_5Cl$ | 0.11 - 0.70 | | | " | $a$ | 9.13 | -4 | | | | | " |
| | | | | | | | $b$ | 7.63 | -5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .7 | $N_2CHCOOC_2H_5 + CHCl_2COOH$ | $C_6H_6$ | $10^3A = 7.5 - 11$ | | | $kA$ | 15 | | | | | | * | (2) |
| | | | $10^2B = 2.5 - 11.4$ | | $k = aB^2 + bB$ | | $a$ | 5.57 | -2 | | | | | |
| | | | | | | | $b$ | 1.40 | -3 | | | | | |
| | | $C_6H_5CH_3$ | $B = 0.033 - 0.25$ | | | " | 25.0 | | | | | | * | (6) |
| | | | | | | | $a$ | 4.50 | -1 | | | | | |
| | | | | | | | $b$ | 4.18 | -2 | | | | | |
| | | $C_6H_5NO_2$ | 0.051 - 0.16 | | | " | $a$ | 2.50 | -1 | | | | | " |
| | | | | | | | $b$ | 1.03 | -2 | | | | | |
| | | $C_6H_5Cl$ | 0.033 - 0.25 | | | " | $a$ | 4.25 | -1 | | | | | |
| | | | | | | | $b$ | 5.18 | -2 | | | | | |
| | | $C_6H_5Br$ | 0.036 - 0.27 | | | " | $a$ | 4.18 | -1 | | | | | |
| | | | | | | | $b$ | 8.68 | -2 | | | | | |
| | | $C_6H_5I$ | 0.046 - 0.19 | | | " | $a$ | 5.50 | -1 | | | | | |
| | | | | | | | $b$ | 6.50 | -2 | | | | | |
| .8 | $N_2CHCOOC_2H_5 + CH_2BrCOOH$ | $C_6H_6$ | $10^3A = 7.5 - 11$ | | | $kA$ | 15 | | | | | | * | (2) |
| | | | $10^2B = 3 - 50$ | | $k = aB^2 + bB$ | | $a$ | 3.92 | -4 | | | | | |
| | | | | | | | $b$ | 8.68 | -5 | | | | | |
| | | $C_6H_5CH_3$ | $B = 0.27 - 0.86$ | | | | 25.0 | | | | | | | |
| | | | | | | | $a$ | 2.23 | -4 | | | | * | (6) |
| | | | | | | | $b$ | 3.11 | -5 | | | | | |
| | | $C_6H_5NO_2$ | 0.40 - 1.3 | | | | $a$ | 7.32 | -4 | | | | | " |
| | | | | | | | $b$ | 3.83 | -4 | | | | | |
| | | $C_6H_5Cl$ | 0.16 - 0.99 | | | | $a$ | 4.03 | -4 | | | | | " |
| | | | | | | | $b$ | 3.57 | -5 | | | | | |
| | | $C_6H_5Br$ | 0.33 - 1.1 | | | | $a$ | 4.41 | -4 | | | | | " |
| | | | | | | | $b$ | 4.16 | -5 | | | | | |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .9 | $N_2CHCOOC_2H_5 + CH_3CHBrCOOH$ | $C_6H_6$ | $10^3A = 7.5 - 11$<br>$10^2B = 9 - 50$ | | | $kA$ | 15 | | | | | | * | (2) |
| | | | | | $k = aB^2 + bB$ | | $a$ | 2.64 | -5 | | | | | |
| | | | | | | | $b$ | 2.92 | -6 | | | | | |
| .10 | $N_2CHCOOC_2H_5 + CH_2ICOOH$ | $C_6H_5Cl$ | $B = 0.17 - 0.14$ | | | $kA$ | 25.0 | | | | | | | |
| | | | | | $k = aB^2 + bB$ | | $a$ | 8.82 | -5 | | | | * | (6) |
| | | | | | | | $b$ | 8.90 | -6 | | | | | |
| .11 | $N_2CHCOOC_2H_5 + (NO_2)_3C_6H_2COOH$ | $C_6H_6$ | $10^3A = 7.5 - 11$;<br>$B = 0.068$<br>$0.136$ | | | $kA$ | 15<br>" | 4.9<br>1.1 | -7<br>-6 | | | | * | (2) |

## COMMENTS

**(.1)** Variation of $k$ with $[H^+]$ is representable ([10]) by $k = (a/[H^+]) + b + c[H^+]$, where $a$ (not evaluated) is not necessarily zero; at 10.1°C, $b = 0.124$ and $c = 0.525$. The temperature variation of $k$ is representable ([10]) by $k = 4.27 \times 10^{12} e^{-17500/RT}$ or by $\ln k = 44.6801 - 4.615 \ln T - 18890/RT$. The first order in A and in $[H^+]$ is well followed in $HNO_3$, but $k$ falls with the progress of the reaction in HCl at $A \geqslant 0.01$, owing to the substitution side reaction $A + HCl \rightarrow N_2 + CH_2ClCOOC_2H_5$ which consumes the catalyst. The value of $k$ in $H_2O$ solution, defined by the rate law $kA[H^+]$, at 25°C, is $k = 6.42 \times 10^{-1}$, in very good agreement between ([7]) ( $[H^+] = 0.002$–$0.015$), ([3]) (0.0009–0.09), and ([10]) (at high $[H^+]$). **(.1.1)** Agreement of the value of $k$ in $H_2O$ at 25°C, $6.50 \times 10^{-1}$, with the $6.42 \times 10^{-1}$ of ([10]) ([7]) ([2]), indicates that these first - order $k$ refer to $[H^+] = 1M$. Picric-acid catalyzed reaction with $H_2O$, at different concentrations of the acid, in $H_2O + D_2O$ mixtures, see ([4]). **(.2) (.3) (.4) (.5)** For the reactions with

## COMMENTS *(continued)*

alcohol in alcohol-water solvents, up to $[H_2O] = 3\ M/l$, the first - order $k$ (in A) is representable by $k = K/(r + N)$, where $N$ = concentration of $H_2O$ (in $M/l$), $K$ = constant proportional to the concentration and the degree of dissociation of the catalyzing acid, and $r = [BH^+][H_2O]/[B][H_3O^+]$. This equation, analogous to the Goldschmidt equation obtaining in esterification of carboxylic acids (see Comments, 202.441) expresses the retardation of the reaction with the alcohol by $H_2O$, owing to a competition between $H_3O^+$ and $BH^+$ ($=ROH_2^+$) assumed to be rate determining through the step $A + ROH_2^+ \rightarrow N_2 + ROCH_2COOC_2H_5 + H^+$. The values of $r$ are: $r = 0.15$, for both $N_2CHCOOCH_3$ and $N_2CHCOOC_2H_5$, and $CCl_3COOH$, $(NO_2)_3C_6H_2COOH$, $HSO_3C_6H_3(OH)COOH$.

| ([8]) Reaction | $(NO_2)_3C_6H_2OH$ | $r$ |
|---|---|---|
| (.3) | 0.00909 | 0.63 |
| | 0.00455 | 0.55 |
| | 0.00227 | 0.49 |
| (.4) | 0.00909 | 0.14 |
| | 0.00455 | 0.16 |
| | 0.00227 | 0.15 |
| (.5) | 0.00909 | 0.12 |

For (.4), satisfactory agreement between ([1]) and ([8]). All acid-catalyzed reactions in alcohol-water mixtures are accompanied by side reactions with the acid itself. Further data on reaction (.4) catalyzed by $(NO_2)_3C_6H_2COOH$ plus picrates, see ([11]); the first-order $k = [\gamma k_H + (1 - \gamma) k_M]\ c$, where $c$ = concentration of the acid, $\gamma$ = degree of dissociation, $k_H$ and $k_M$ corresponding, respectively, to the catalytic effects of the dissociated and the undissociated parts of the acid. The alleged catalysis by undissociated picric acid is considered inconclusive by ([2]). (.6) (.7) (.8) (.9) (.10) The first-order law in A is justified by near constancy of the acid concentration (not over 8% change) ([2]). The second-order term in the acid is interpreted as acceleration of the reaction by dissociation of dimeric acid molecules ([2]). Original ([2]) gives further data for pairs of acids, and for acid catalysis in the presence of $C_2H_5OH$ and $C_6H_5OH$. The effective apparent order in B in the aprotic solvents ranges from 1.3 to 1.9 ([6]).

## LITERATURE

(1) H. Braune, *ZPC* 1913, **85**, 170. (2) J.N.Brönsted, R.P.Bell, *ACS* 1931, **53**, 2478. (3) W. Fraenkel, *ZPC* 1907, **60**, 202, 207. (4) Ph. Gross, H.Steiner, F. Krauss, *TFS* 1936, **32**, 877. (5) Ph. Gross, H. Steiner, F. Krauss, *TFS* 1938, **34**, 351. (6) R.J. Hartman, C. J . Hochanandel, E.G.Bobalek, *ACS* 1946, **68**, 2071. (7) B.Holmberg, *ZPC* 1908, **62**, 726. (8) W.S.Millar, *ZPC* 1913, **85**, 129. (9) E.A.Moelwyn-Hughes, P. Johnson, *TFS* 1940, **36**, 949. (10) E.A.Molewyn-Hughes, P.Johnson, *TFS* 1941 **37**, 282. (11) H.C.S. Snethlage, *ZPC* 1913, **85**, 211.

# SOLVOLYSIS

## of $N_2$:C bond by aromatic carboxylic acids

*Liquid phase*

Reaction type $N_2CR_2 + ArCOOH \rightarrow N_2 + ArCOOCHR_2$

(A) (B) (L) (M)

Method Measurement of $N_2$ evolved

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $N_2C(p-C_6H_4CH_3)_2 + C_6H_5COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 1.06 | -3 |
| .2 | $N_2C(p-C_6H_4CH_3)_2 + o-CH_3C_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 4.22 | -3 |
| .3 | $N_2C(p-C_6H_4CH_3)_2 + m-CH_3C_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 6.32 | -3 |
| .4 | $N_2C(p-C_6H_4CH_3)_2 + o-CH_3OC_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 4.65 | -5 |
| .5 | $N_2C(p-C_6H_4CH_3)_2 + o-OHC_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | ~ 3 | -1 |
| .6 | $N_2C(p-C_6H_4CH_3)_2 + o-NO_2C_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 8.78 | -3 |
| | | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$ AB | 25 | 5.48 | -3 |
| .7 | $N_2C(p-C_6H_4CH_3)_2 + m-NO_2C_6H_4COOH$ | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$ AB | 25 | 5.62 | -3 |
| .8 | $N_2C(p-C_6H_4CH_3)_2 + p-NO_2C_6H_4COOH$ | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$ AB | 25 | 4.75 | -3 |
| .9 | $N_2C(p-C_6H_4CH_3)_2 + o-ClC_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 1.74 | -2 |
| .10 | $N_2C(p-C_6H_4CH_3)_2 + m-ClC_6H_4COO$ | $C_7H_8$ | A = B ~ 0.03 | $k$ AB | 25 | 1.02 | -2 |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .11 | $N_2C(p-C_6H_4CH_3)_2 + p-ClC_6H_4COOH$ | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$AB | 25 | 5.90 | -5 |
| .12 | $N_2C(p-C_6H_4CH_3)_2 + o-BrC_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$AB | 25 | 2.30 | -2 |
| | | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$AB | 25 | 1.45 | -2 |
| .13 | $N_2C(p-C_6H_4CH_3)_2 + m-BrC_6H_4COOH$ | $C_7H_8$ | A = B ~ 0.03 | $k$AB | 25 | 1.08 | -2 |
| | | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$AB | 25 | 1.25 | -3 |
| .14 | $N_2C(p-C_6H_4CH_3)_2 + p-BrC_6H_4COOH$ | $CH_3COOC_2H_5$ | A = B ~ 0.03 | $k$AB | 25 | 6.52 | -4 |

## LITERATURE

J. F. Norris, W. H. Strain *ACS* 1935, 57, 187

# SOLVOLYSIS

## Aromatic acyl halides

*Liquid phase*

Reaction type $ArCOX + ROH \rightarrow ArCOOR + HX$

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, at the end of the table.

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 4.3 | -4 | (1) |
| .2 | $C_6H_5COCl + CH_3OH$ | B | | $kA$ | 0 | 4.4 | -4 | (2) |
| | | | | | 25 | 4.25 | -3 | |
| .3 | $C_6H_5SO_2Cl + H_2O$ | An50 | 0.04 | $kA$ | 25 | 2.4 | -4 | (1) |
| | | Et50 | 0.02 | $kA$ | 25 | 5.2 | -4 | (1) |
| .4 | $o - CH_3C_6H_4COCl + H_2O$ | An50 | 0.02 | | 0 | very fast | | (1) |
| .5 | $o - CH_3C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 2.28 | -3 | (2) |
| .6 | $o - CH_3C_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 25 | 3.48 | -3 | (2) |
| .7 | $m - CH_3C_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 6.3 | -4 | (1) |
| .8 | $m - CH_3C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 4.93 | -4 | (2) |
| .9 | $m - CH_3C_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0 | 6.28 | -5 | (2) |
| | | | | | 25 | 7.88 | -4 | |
| .10 | $p - CH_3C_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 1.25 | -3 | (1) |



942151 O—51——19

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .11 | $p - CH_3C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 3.0 | -4 | (2) |
| .12 | $p - CH_3C_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 25 | 6.0 | -4 | |
| .13 | $2,4,6 - (CH_3)_3C_6H_2COCl + CH_3OH$ | B | | $kA$ | 0 | very fast | | (2) |
| .14 | $p - C_6H_5C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 3.3 | -4 | (2) |
| .15 | $p - CH_3C_6H_4SO_2Cl + H_2O$ | An50 | 0.04 | $kA$ | 25 | 1.8 | -4 | (1) |
| | | Et50 | 0.02 | $kA$ | 25 | 4.45 | -4 | " |
| .16 | $o - CH_3OC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0 | 2.12 | -3 | (2) |
| .17 | $m - CH_3OC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0 | 7.69 | -5 | (2) |
| .18 | $o - NO_2C_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 7.7 | -4 | (1) |
| .19 | $o - NO_2C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 7.9 | -4 | (2) |
| .20 | $o - NO_2C_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 25 | 1.22 | -3 | (2) |
| .21 | $m - NO_2C_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 3.0 | -3 | (1) |
| .22 | $m - NO_2C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 5.48 | -3 | (2) |
| .23 | $p - NO_2C_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 5.0 | -3 | (1) |
| .24 | $p - NO_2C_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 6.88 | -3 | (2) |
| .25 | $2,4,6 - (NO_2)_3C_6H_2COCl + CH_3OH$ | B | | $kA$ | 25 | very slow | | (2) |
| .26 | $m - NO_2C_6H_4SO_2Cl + H_2O$ | An50 | 0.04 | $kA$ | 25 | 7.3 | -4 | (1) |
| | | Et50 | 0.02 | $kA$ | 25 | 9.7 | -4 | (1) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | Literature |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | |
| .27 | o - $ClC_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 6.3 | -4 | (1) |
| .28 | o - $ClC_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 1.23 | -3 | (2) |
| .29 | o - $ClC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 25 | 2.1 | -3 | (2) |
| .30 | m - $ClC_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 6.3 | -4 | (1) |
| .31 | m - $ClC_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 1.48 | -3 | (2) |
| .32 | m - $ClC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0<br>25 | 4.10<br>2.57 | -4<br>-3 | (2) |
| .33 | p - $ClC_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 3.7 | -4 | (1) |
| .34 | p - $ClC_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 7.19 | -4 | (2) |
| .35 | p - $ClC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 25 | 1.21 | -3 | (2) |
| .36 | o - $BrC_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 5.8 | -4 | (1) |
| .37 | o - $BrC_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 1.22 | -3 | (2) |
| .38 | m - $BrC_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 7.3 | -4 | (1) |
| .39 | m - $BrC_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 1.53 | -3 | (2) |
| .40 | p - $BrC_6H_4COCl + H_2O$ | An50 | 0.02 | $kA$ | 0 | 4.0 | -4 | (1) |
| .41 | p - $BrC_6H_4COCl + CH_3OH$ | B | | $kA$ | 0 | 8.0 | -4 | (2) |
| .42 | o, o -$Br_2C_6H_3COCl + H_2O$ | An50 | 0.01 | $kA$ | 0<br>25 | 4.8<br>6.8 | -6<br>-5 | (3) |

| No. | Reaction | Medium (Solvent) | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .43 | $o, p - Br_2C_6H_3COCl + H_2O$ | An50 | 0.004 | $kA$ | 0 | 9.2 | -4 | (3) |
| .44 | $m, m - Br_2C_6H_3COCl + H_2O$ | An50 | 0.004 | $kA$ | 0 | 5.8 | -3 | (3) |
| .45 | $2,4,6 - Br_3C_6H_2COCl + CH_3OH$ | B | | $kA$ | 25 | 3.1 | -6 | (2) |
| .46 | $o - IC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0 | 2.12 | -4 | (2) |
| .47 | $m - IC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0 | 3.0 | -4 | (2) |
| .48 | $p - IC_6H_4COCl + C_2H_5OH$ | B | | $kA$ | 0 | 1.39 | -4 | (2) |

## SOLVENTS

| | |
|---|---|
| An50 | $(CH_3)_2CO$ 50 vol % + $H_2O$ 50 vol % |
| Et50 | $C_2H_5OH$ 50 vol % + $H_2O$ 50 vol % |
| B | The second reactant is the solvent (in great excess) |

## LITERATURE

(1) G. Berger, S.C.J. Olivier, *RTC*, 1927, **46**, 516.
(2) J.F.Norris, H.H.Young, *ACS* 1935, **57**, 1420.
(3) S.C.J. Olivier, *RTC* 1929, **48**, 227.

# SOLVOLYSIS

## CN halides

*Liquid phase*

**Homogeneous Reactions**
**242.570.**

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CNBr + OH^- \rightarrow CNOH + Br^-$ | $H_2O$ | $10^3A = 0.6 - 6$; $10^3B = 3 - 12$ | | | $k$ AB | 0.2 | 9.7 | −2 | |
| | $(CNBr + 2OH^- \rightarrow CNO^- + Br^- + H_2O)$ | | 1.8 − 6; 3 − 6 | | | " | 10 | 2.7 | −1 | |
| | | | 0.8 − 1.6; 2 − 6 | | | " | 20 | 7.0 | −1 | 15.3 |
| .2 | $CNI + OH^- \rightarrow CNOH + I^-$ | $H_2O$ | $10^3A = 5$; $10^3B = 10$ | | | $k$ AB | 20 | 7.4 | −3 | |
| | $(CNI + 2OH^- \rightarrow CNO^- + I^- + H_2O)$ | | " 165 | | | | " | 5.2 | −3 | |
| | | | " 41 | | | | 0.2 | 5.9 | −4 | |
| | | | | | | | 20 | 6.9 | −3 | |
| | | | | | | | 30 | 2.05 | −2 | 19.5 |
| | | | $10^3A = 5$; $10^3B = 82$ | | | $k$ AB | 20 | 6.2 | −3 | |
| | | | | $NaNO_3$ | 0.1 | " | " | 6.05 | −3 | |
| | | | | KCl | " | " | " | 6.0 | −3 | |
| | | | | KI | " | " | " | 5.75 | −3 | |
| | | | | KCN | " | " | " | 4.95 | −3 | |

## LITERATURE

R. O. Griffith, R. S. Jobin, A. McKeown, *TFS* 1938, 34, 316.

# SOLVOLYSIS

## P – O bond

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $(OH)_2OP-O-PO(OH)_2 + H_2O \rightarrow 2\,(OH)_3PO$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | pH | $k = k^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ |
| .1 | $Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4$ | $H_2O$ | 0.012 | $k$ A | 100 | 9.33 | 1.7 | −6 |
| .2 | $Na_3P_2O_7 + H_2O \rightarrow Na_2HPO_4 + NaH_2PO_4$ | " | " | " | " | 7.34 | 7.8 | −5 |
| .3 | $Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4$ | " | " | " | " | 3.21 | 1.44 | −4 |
| .4 | $NaH_3P_2O_7 + H_2O \rightarrow NaH_2PO_4 + H_3PO_4$ | " | " | " | " | 2.07 | 2.40 | −4 |
| .5 | $H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$ | " | " | " | " | 1.92 | 8.30 | −4 |

## LITERATURE

L. M. Postnikov, *Vestnik Moskov. Univ.* 1950, 5, No. 5, 63.

# ISOTOPE EXCHANGE

*Liquid phase*

## H - D exchange on aliphatic C

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_5OH + HDO \rightarrow C_2H_5OD + H_2O$ | $H_2O$ | B = 20 % | | | $kAB$ | 25.0 | | 2.4 ±0.2 | -6 | | | | * | ([5]) |
| .2 | $C_2H_5OD + H_2O \rightarrow C_2H_5OH + HDO$ | $H_2O$ | | | | $kAB$ | 25.0 | | 2.2 ±0.2 | -6 | | | | * | ([5]) |
| .3 | $CH_3COCH_3 + D_2O \rightarrow CH_2DCOCH_3 + HDO$ | $H_2O$ + B; | A = | $[OH^- + OD^-]$ = | | $kA[OD^- + OH^-]$ | | | | | | | | | ([7]) |
| | | % D = 99.6 | 1.5 | 0.003 - 0.0086 | | | 25 | | 3.6 | -5 | | | | | |
| | | " | " | 0.0014 | | | " | | 2.9 | -5 | | | | | |
| | | 97.5 | 3.2 | 0.006 | | | " | | 3.2 | -5 | | | | | |
| | | 92.6 | 1.7 | " | | | " | | 2.5 | -5 | | | | | |
| | | 51.6 | 1.6 | " | | | " | | 4.5 | -6 | | | | | |
| .4 | $CD_3COOH + H_2O \rightarrow CD_2HCOOH + H_2O$ | $H_2O$; | A = 0.14 - 2.5 | | - | $kA$ | 183 | | 1.8 | -5 | | | | | ([1]) |
| | | pH > 8.5 | | | | | 206 | | 9.2 | -5 | 32 | | | | |
| | | | A = 0.22 - 0.77 | HCl = 0.15 - 0.8 | | $kA[HCl]$ | | | | | | | | | " |
| | | pH < 2.5 | | | | | 183 | | 2.3 | -4 | | | | | |
| | | | | | | | 206 | | 1.06 | -3 | 26 | | | | |
| | | | A = 0.3 - 2.0 | KOH = 0.04 - 1.0 | | $kA[OH^-]$ | | | | | | | | | " |
| | | pH > 8.5 | | | | | 183 | | 1.4 | -3 | | | | | |
| | | | | | | | 206 | | 5.4 | -3 | 22 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $CH_3COOD + D_2O \longrightarrow CH_2DCOOD + HDO$ | $D_2O$; pH > 8.5 | A = 0.5 - 2.8 | | - | $kA$ | 183 | | 3.5 | -5 | | | | | (1) |
| | | | | | | | 206 | | 2.0 | -3 | | | | | |
| | | A = 0.5 - 1.8; pH < 2.5 | | DCl = 0.3 - 2.0 | | $kA[DCl]$ | 183 | | 4.8 | -4 | | | | | (1) |
| | | | | | | | 206 | | 1.8 | -3 | | | | | |
| | | A = 0.4 - 1.0; pH > 8.5 | | KOD = 0.03 - 3.1 | | $kA[OD^-]$ | 183 | | 3.1 | -3 | | | | | (1) |
| | | | | | | | 206 | | 6.6 | -3 | | | | | |
| .6 | $CH_2{:}CHCH_2COO^- + HDO \longrightarrow CH_2{:}CHCHDCOO^- + H_2O$ | $H_2O + D_2O$ 2.5 % | A = 1.0 | NaOH | 1.05 | $kA$ | 100 | | 1.5 | -4 | | | | * | (3) |
| .7 | $C_6H_5COCH(CH_3)C_2H_5 + OD^- \longrightarrow C_6H_5COCD(CH_3)C_2H_5 + OH^-$ | dioxane + $D_2O$ ~ 1.5 (M/l) | A ~ 0.3; B ~ 0.125 | | | | 35.0 | | | | | | | * | (2) |
| | | | | | | | (0.10) | | $3.6 \times 10^3$ | | | | | | |
| | | | | | | | (0.25) | | $7.2 \times 10^3$ | | | | | | |
| | | | | | | | (0.41) | | $1.4 \times 10^4$ | | | | | | |
| | | | | | | | (0.57) | | $2.3 \times 10^4$ | | | | | | |
| .8 | $p - CH_3C_6H_4CH(C_6H_5)COO^- + D_2O \longrightarrow p - CH_3C_6H_4CD(C_6H_5)COO^- + HDO$ | $H_2O$; B = 3 % | A + L = 0.2 | NaOH | 0.22 | $kA$ | 100 | | 2.2 | -6 | | | | * | (4) |
| .9 | $p - CH_3C_6H_4CD(C_6H_5)COO^- + H_2O \longrightarrow p - CH_3C_6H_4CH(C_6H_5)COO^- + HDO$ | $H_2O$ | A + L = 0.2 | NaOH | 0.22 | $kA$ | 100 | | 1.4 | -6 | | | | * | (4) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .10 | $p - CH_3OC_6H_4CH{:}NCH_2C_6H_5 + C_2H_5OD \longrightarrow$ | $C_2H_5OH$ + B | A + L = 1.78 | | | | 74.0 | | | | | | | * | (6) |
| | $\left\{ \begin{array}{l} p - CH_3OC_6H_4CH{:}NCHDC_6H_5 \\ p - CH_3OC_6H_4CHD.N{:}CHC_6H_5 \end{array} \right\} + C_2H_5OH$ etc. | 31.5 mole % | | $OC_2H_5^-$ | 0.1 | | (0.045) | 1.44 × $10^4$ | | | | | | | |
| | | | | | | | (0.0845) | 2.88 × $10^4$ | | | | | | | |
| | | | | | | | (0.188) | 8.64 × $10^4$ | | | | | | | |
| | | | | | | | (0.628) | 2.68 × $10^6$ | | | | | | | |
| | | 94.4 " | | " | " | | (0.054) | 1.8 × $10^3$ | | | | | | | |
| | | | | | | | (0.126) | 3.6 × $10^3$ | | | | | | | |

## COMMENTS

**(.1) (.2)** Rate determining step $C_2H_5OH + HDO \underset{b}{\overset{a}{\rightleftharpoons}} C_2H_5OHD^+ + OH^-$, gives, on the assumption $k_b \equiv$ collision frequency, $k_a = 2.8 \times 10^{-6}$. **(.6)** Data corrected for irreversible isomerization to $CH_2DCH{:}CHCOO^-$, $CH_3CH{:}CHCDCOO^-$, and $CH_2DCH{:}CDCOO^-$; $k$ for H - D exchange is 1.55 × $k$ for isomerization to crotonic acid. Mechanism $A + OH^- \longrightarrow CH_2{:}CH\bar{C}HCOO^- + H_2O$; $CH_2{:}CH\bar{C}HCOO^- + HDO \longrightarrow CH_2{:}CHCHDCOO^- + OH^-$. **(.7)** Assuming 12-fold transfer rate of protons, exchange rate is identical with racemization rate. **(.8) (.9)** Accompanied by racemization; ionic mechanism. **(.10)** Data refer to exchange of one H atom per molecule.

## LITERATURE

(1) I.D.C.Bok, K.H.Geib, *ZPA*[A] 1939, **183**, 353. (2) S.K.Hsu, C.K.Ingold, C.L.Wilson, *CSL* **1938**, 78. (3) D.J.G.Ives, *CSL* **1938**, 91. (4) D.J.G.Ives, G.C.Wilks, *CSL* **1938**, 1455. (5) W.J.C.Orr, *TFS* 1936, **32**, 1033. (6) E.de Salas, C.L.Wilson, *CSL* **1938**, 319. (7) W.D.Walters, K.F.Bonhoeffer, *ZPC*[A] 1938, **182**, 265.

# ISOTOPE EXCHANGE

## H - D exchange on aromatic C

*Liquid phase*

The position of the substitution is indicated in parentheses after the arrow.

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | Fractional time | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | $A = A^0 \times 10^n$ $A^0$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2,4,6 - CD_3H(OD)_2 - 1,3 + H_2O \longrightarrow$ (2) | $H_2O$ | A + L = 0.01 - 0.6 | HCl | 0.01 - 0.1 | $kA[HCl]$ | 64.7 | | 1.55 | -1 | | | | * | (1) |
| | $\longrightarrow$ (4) or (6) | " | " | " | " | " | " | | 1.55 | -1 | 20.6 | 3 | 11 | | " |
| | | | | | | | | | | | (34.7 - 100 °C) | | | | |
| .2 | $C_6H_3(OD)_3 - 1,2,3 + H_2O \longrightarrow$ (5) | $H_2O$ | A + L = 0.16 | HCl | 0.01 - 2.3 | $kA[HCl]$ | 64.7 | | 3 | -4 | | | | * | (1) |
| | $\longrightarrow$ (4) or (6) | " | " | " | " | " | " | | 5.5 | -1 | 19 | | | | " |
| .3 | $C_6H_3(OH)_3 - 1,3,5 + D_2O$ | $D_2O$ 0.995 | A/B = 1 | NaOH | 0.1 | | 100 | | | | | | | * | (2) |
| | | | | | | (0.995 → 0.28) | | $9.0 \times 10^3$ | | | | | | | |
| | | | | | | (0.995 → 0.27) | | $1.8 \times 10^4$ | | | | | | | |
| | | | | | | (0.995 → 0.26) | | ∞ | | | | | | | |

## COMMENTS

In all cases, hydroxyl-D is exchanged for H instantaneously.

**(.1) (.2)** Data of fractional times for the uncatalyzed, the NaOH-, and the $CH_3COOH + CH_3COONa$-catalyzed reactions, and for the exchange $m - C_6H_4(OH)_2 + D_2O$, in original ([1]).

**(.3)** The bold-face decimal fractions refer to the fall of the fraction of $D_2O$ in the solvent from the initial fraction 0.995. At the limit ($D_2O$ in solvent = **0.26**), the number of H atoms exchanged is ~ 5.5.

## LITERATURE

([1]) K. H. Geib, *ZPC*[A] 1937, **180**, 211.

([2]) F. K. Munzberg, *ZPC*[B] 1936, **33**, 26.

# ISOTOPE EXCHANGE

## Oxygen isotope exchange



Amounts are in M/l. Rate and mass-action of A and L are in M/l per second and M/l of A and L, or in atom fraction $O^{18}/O$ per second and atom fraction of A and L.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CO^{18}O^{18}H + H_2O^{16} \rightarrow C_6H_5CO^{16}O^{18}H + H_2O^{18}$ | $H_2O$ | $C_6H_5COOH$ = 0.05 - 0.10 | HCl | 0.1 - 0.5 | $k$ (A - L) $[H^+]$ | 80 | 2.34 | -4 |

## COMMENTS

The same rate law and the same $k$ is valid for the reverse reaction. No effect of KCl.

## LITERATURE

J. Roberts, H.C. Urey, *ACS* 1939, **61**, 2580.

# ISOTOPE EXCHANGE

## Halogen for halogen, in organic compounds

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Coded solvents, see at the end of the table.

Reaction types $RX + X^{*-} \rightarrow RX^{*} + X^{-}$
(A) (B) (L) (M)

*or* $RX + 1/2\ X_2^{*} \rightarrow RX^{*} + 1/2\ X_2$

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^{o} \times 10^{n}$ $k^{o}$ | $n$ | $E$ | $A = A^{o} \times 10^{n}$ $A^{o}$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Aliphatic carbon** | | | | | | | | |
| .1 | $C_2H_5I + I^{*-}$ | $C_2H_5OH$ | (A + L) = 0.02; (B + M) = 0.017 | | | $k$ AB | 50 | 4.8 | -5 | | | | * | (13) |
| | | | | | | | 60 | 1.3 | -4 | | | | | |
| | | | | | | | 70 | 3.45 | -4 | 21.3 | 5.3 | 8 | | |
| | | $C_2H_5OH$ | (A + L) = (B + M) = 0.1 | | | $k$ AB | 10 | 2.3 | -5 | | | | * | (11) |
| | | | | | | | 20 | 9.2 | -5 | | | | | |
| | | | | | | | 30 | 2.15 | -4 | | | | | |
| | | | | | | | 40 | 4.2 | -4 | | | | | |
| | | | | | | | 80 | 1.5 | -2 | 19.0 | | | | |
| .2 | *trans*-CHI:CHI + 1/2 $I_2^{*}$ | decalin | A = 0.005 - 0.03; B = 0.003 - 0.013 | | | $k$ $AB^{1/2}$ | 100 | 1.0 | -1 | 26 | 6.6 | 12 | * | (12) |
| .3 | $C_3H_7Br + Br^{*-}$ | An 90 | (A + L) = 0.05-0.1; (B + M) = 0.03- 0.06 | | | $k$ AB | 0 | 1.6 | -5 | | | | | (9) |
| | | | | | | | 25 | 3.7 | -4 | | | | | |
| | | | | | | | 34.5 | ~ 1.0 | -3 | | | | | |
| | | | | | | | 65.6 | ~ 1.3 | -2 | 18.1 | | | | |



942151 O—51——20

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .4 | $(CH_3)_2CHBr + Br^{*-}$ | $(CH_3COOCH_2)_2$ | (A + L) = 0.05-0.1; (B + M) = 0.03-0.06 | | | $k$ AB | 40 | 1.5 | −6 | | | | | ([10]) ([8]) |
| | | | | | | | 80 | 5.0 | −5 | | | | | |
| | | | | | | | 100 | 2.6 | −4 | | | | | |
| | | | | | | | 140 | ~ 4 | −3 | 19.7 | | | | |
| | | An 90 | " " | | | $k$ AB | 25 | 1.2 | −5 | | | | | " |
| | | | | | | | 34 | 3.9 | −5 | | | | | |
| | | | | | | | 44 | 1.37 | −4 | | | | | |
| | | | | | | | 70 | 2.27 | −3 | 22.9 | | | | |
| .5 | $(CH_3)_2CHBr + 1/2\ Br_2^*$ | An 90 | (A + L) = 0.15; (B + M) = 0.03-0.07 | | | $k\ AB^{1/2}$ | 25 | 1.2 | −5 | | | | | ([3]) |
| | | | | | | | 44.5 | 1.37 | −4 | | | | | |
| | | | | | | | 70 | 2.27 | −3 | 23 | 4.7 | 10 | | |
| .6 | $CH_3CHBrCOOH + Br^{*-}$ | $(CH_3)_2CO$ | (B + M) = 0.3 | | | $k$ AB | 22 | 5.15 | −4 | | | | | ([2]) |
| | | $H_2O$ | (A + L) ~ 0.03; (B + M) = 0.002-0.04 | | | $k$ AB | | | | | | | | |
| | | | | $H_2SO_4$ | 1 | | 60 | 2.0 | −4 | | | | | ([6]) |
| | | | | | | | 70 | 5.0 | −4 | | | | | |
| | | | | | | | 80 | 1.15 | −3 | | | | | |
| | | | | | | | 100 | 6.4 | −3 | 20.9 | 9 | 7 | | |
| .7 | $C_3H_7I + I^{*-}$ | $C_2H_5OH$ | (A + L) = 0.02; (B + M) = 0.017 | | | $k$ AB | 50 | 3.25 | −5 | | | | * | ([13]) |
| | | | | | | | 60 | 8.84 | −5 | | | | | |
| | | | | | | | 70 | 2.27 | −4 | 20.8 | 2.1 | 8 | | |
| .8 | $(CH_3)_2CHI + I^{*-}$ | $C_2H_5OH$ | (A + L) = 0.02; (B + M) = 0.017 | | | $k$ AB | 45 | 1.0 | −6 | | | | * | ([13]) |
| | | | | | | | 60 | 5.0 | −6 | 23.8 | 1.3 | 9 | | |
| .9 | $(CH_3)_3CCl + Cl^{*-}$ | HCOOH | | | | $k$ A | 15 | 3 | −4 | | | | | ([7]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .10 | $C_4H_9Br + Br^{*-}$ | $(CH_3COOCH_2)_2$ | (A + L) = 0.05-0.1; (B + M) = 0.03-0.06 | | | $k$ AB | 25 | 1.1 | −5 | | | | | ([10]) ([8]) |
| | | | | | | | 50 | 1.15 | −4 | | | | | |
| | | | | | | | 80 | 1.3 | −3 | | | | | |
| | | | | | | | 100 | ~ 5.2 | −2 | 17.8 | | | | |
| | | $(CH_3)_2CO$ | " " | | | " | −10 | 9.0 | −6 | | | | | " |
| | | | | | | | 0 | 4.6 | −5 | | | | | |
| | | | | | | | 20 | 1.0 | −3 | | | | | |
| | | | | | | | 40 | ~ 4.5 | −2 | 19.8 | | | | |
| | | An 90 | " " | | | " | 34.5 | 9.0 | −5 | | | | | " |
| | | | | | | | 44.5 | 2.3 | −4 | 18.9 | | | | |
| .11 | $C_4H_9Br + 1/2\ Br_2^*$ | An 90 | (A + L) < 0.15; (B + M) < 0.15 | | | $k\ AB^{1/2}$ | 0 | 1.7 | −6 | | | | * | ([8]) |
| | | | | | | | 25 | 3.3 | −5 | | | | | |
| | | | | | | | 65 | 1.5 | −3 | | | | | |
| .12 | $(CH_3)_2CHCH_2Br + 1/2\ Br_2^*$ | An 90 | (A + L) = 0.1-0.2; (B + M) = 0.03-0.06 | | | $k\ AB^{1/2}$ | 25 | 1.4 | −5 | | | | | ([3]) |
| | | | | | | | 49 | 2.4 | −4 | | | | | |
| | | | | | | | 70 | 1.7 | −3 | 20.2 | 7.1 | 8 | | |
| .13 | $(CH_3)_3CBr + Br^{*-}$ | $(CH_3COOCH_2)_2$ | (A + L) = 0.05-0.1; (B + M) = 0.03-0.06 | | | $k$ AB | 40 | 5.0 | −6 | | | | | ([10]) |
| | | | | | | | 60 | 1.0 | −4 | | | | | |
| | | | | | | | 80 | 2.1 | −4 | | | | | |
| | | | | | | | 100 | ~ 2.4 | −3 | | | | | |
| | | | | | | | 120 | ~ 1 | −2 | 9.3 | | | | |
| .14 | $dl\text{-}C_7H_{15}CH(CH_3)I + I^{*-}$ | $(CH_3)_2CO$ | (A + L) = 0.138; (B + M) = 0.160 | | | $k$ AB | 30 | 1.35 | −3 | | | | * | ([4]) |
| .15 | $d\text{-}C_6H_5CH(CH_3)Br + Br^{*-}$ | $(CH_3)_2CO$ | (A + L) = (B + M) = 0.2 | | | $k$ AB | 30 | 8.70 | −4 | | | | * | ([5]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Aromatic carbon** | | | | | | | | |
| .16 | $p$-$NO_2C_6H_4Cl + Cl^{*-}$ | An 90 | | | | $k$ AB | 30 | 1.81 | -5 | | | | | (1) |
| | | | | | | | 50 | 1.42 | -4 | | | | | |
| | | | | | | | 70 | 1.01 | -3 | 20.8 | 1.8 | 10 | | |
| .17 | $p$-$NO_2C_6H_4Br + Br^{*-}$ | An 90 | | | | $k$ AB | 0 | 1.29 | -3 | | | | | (1) |
| | | | | | | | 15 | 6.43 | -3 | | | | | |
| | | | | | | | 30 | 3.56 | -2 | 18.0 | 3.3 | 11 | | |
| .18 | 2, 4-$(NO_2)_2C_6H_3Br + Br^{*-}$ | $(CH_3COOCH_2)_2$ | (A + L) = 0.05-0.1; (B + M)′ = 0.03-0.06 | | | $k$ AB | 70 | 2.1 | -5 | | | | | (10) |
| | | | | | | | 90 | 1.1 | -4 | | | | | |
| | | | | | | | 100 | 2.4 | -4 | | | | | |
| | | | | | | | 120 | ~ 9 | -4 | | | | | |
| | | | | | | | 130 | ~ 1.6 | -3 | 19.3 | | | | |

## SOLVENTS

An90 $H_2O + (CH_3)_2CO$ 90 vol %.

## COMMENTS

**General.** The halogens marked $X^*$ are radioactive isotopes. The reaction kinetics were followed by G. M. counter. The same rate law and the same second-order rate constant hold for the forward and the reverse reaction; the total rate from left to right is thus expressed by $k$ ( AB - LM ), and $k$ is determined from its integrated form. The sums ( A + L ) and ( B + M ) remain constant throughout the course of the reaction in either direction. (.1) Values of $k$ of ([13]) and ([11]) are not in agreement; $I^*$ ([13]) is $I^{128}$; in ([11]), "a mixture of long-lived isotopes." (.2) $k$ and $A$ converted to M/l from mM/l. Simultaneous isomerization is negligible. The photochemical reaction in hexane at 15 - 50°C follows the same rate law, with E = 8.5. (.6) Reverse reaction proceeds with the same $k$. Walden inversion proceeds with practically the same $k$, consequently, the inversion proceeds over substitution. (.7) (.8) Hydrolysis proceeds over the same mechanism. (.11) Acids and bases have no catalytic effect. (.14) (.15) $k$ calculated ( by the editors ) from the original $N_s$ = constant sum total of all rates of exchanges occurring in the system, and related to the rate by + $dL/dt = N_s$ ( $B/M_o$ ) ( $A/A_o$ ), hence $k = N_s A_o M_o$, where the subscript $_o$ refers to initial amounts. The sum of rates of exchange is equal to the sum of rates of Walden inversions in the same systems; consequently, inversion proceeds over substitution. The reverse reaction proceeds with the same $k$.

## LITERATURE

(1) T.A.Bither, J.M.Sturtevant, H.C.Thomas, *ACS* 1945, **67**, 1562. (2) W.A.Cowdrey, E.D.Hughes, J.P.Newell, C.L.Wilson, *CSL* **1938**, 209. (3) G.A.Elliot, S.Sugden, *CSL* **1939**, 1837. (4) E.D.Hughes, F.Juliusberger, S.Masterman, B.Topley, J.Weiss, *CSL* **1935**, 1525. (5) E.D.Hughes, F.Juliusberger, A.D.Scott, B.Topley, J.Weiss, *CSL* **1936**, 1173. (6) W.Koskoski, R.W.Dodson, R.D.Fowler, *ACS* 1941, **63**, 2149. (7) W.Koskoski, H.Thomas, R.D.Fowler, *ACS* 1941, **63**, 2451. (8) L.J.Le Roux, S.Sugden, *CSL* **1939**, 1279. (9) L.J.Le Roux, S.Sugden, *CSL* **1939**, 1836. (10) L.J.Le Roux, C.S.Lu, S.Sugden, K.Thomson, *CSL* **1945**, 586.

(11) M.B.Neiman, R.V.Protsenko, DAN 1950, **71**, 327. (12) R.M.Noyes, R.G.Dickinson, V.Schomaker, *ACS* 1945, **67**, 1319. (13) H.Seelig, D.E.Hull, *ACS* 1942, **64**, 941.

# EXCHANGE

## H for S on aliphatic carbon

*Gas phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .1 | $CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$ | A = 0.02 - 0.04<br>B = 0.02 - 0.04 | $k$ AB | 550 | 1.1 | 0 | | | |
| | | | | 575 | 1.9 | 0 | | | |
| | | | | 600 | 3.0 | 0 | | | |
| | | | | 625 | 6.4 | 0 | 34.4 | 1.4 | 9 |

## COMMENTS

Flow. Homogeneous in stainless steel. Order based on constancy of $k$ on variation of A/B by a factor of 2.

## LITERATURE

R. A. Fisher, J. M. Smith, *IEC* 1950, 42, 704.

# EXCHANGE

## Hydrogen - Halogen

## Hydrogen halide formation and decomposition

*Gas phase*

Reaction types $H_2 + X_2 \rightarrow 2\ HX$

$2\ HX \rightarrow H_2 + X_2$

Amounts are in M/l.
Rates in M/l per sec.

| No. | Reaction | Method | Amount of reactant | | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .1 | $H_2 + Cl_2 \rightarrow 2\ HCl$ | flow | A/B = 1/3 - 3/1 | | $k\,AB$ | 230 | 1.7 | -1 | | | | * | (12) |
| | | | | | | 240 | 2.5 | -1 | | | | | |
| | | | | | | 250 | 3.7 | -1 | 18 | | | | |
| | | stat; | $10^3A$ | $10^3B$ | $k\,A^2B/L$ | | | | | | | | |
| | | pyrex vessel | 6.70 | 12.4 | | 184 | 6.5 | -3 | | | | * | (11) |
| | | | " | 16.6 | | " | 2.6 | -3 | | | | | |
| | | | 13.6 | 5.85 | | " | 1.4 | -2 | | | | | |
| | | | " | 4.45 | | " | 3.4 | -3 | | | | | |
| | | | " | 6.35 | | " | 1.07 | -2 | | | | | |
| | | | 6.90 | 17.0 | | " | 2.6 | -3 | | | | | |
| | | stat; | 5.50 | 11.6 | $k\,AB^{1/2}$ | 184 | 1.59 | -3 | | | | * | (11) |
| | | KCl-coated vessel | 10.8 | 11.4 | | " | 9.6 | -4 | | | | | |
| | | | 16.0 | 6.7 | | " | 7.9 | -4 | | | | | |
| | | | 10.8 | 11.6 | | " | 3.4 | -4 | | | | | |

| No. | Reaction | Method | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $H_2 + Br_2 \rightarrow 2\ HBr$ | stat anal(B) | 0.006 - 0.04 | $k\,AB^{1/2}/[m + (L/B)]$ | | | $k$ | | | | | |
| | | | | | 225.7 | 9.93 | -5 | | | | * | (16) |
| | | | | | 251.4 | 8.02 | -4 | | | | | " |
| | | | | | 275.8 | 3.86 | -3 | | | | | (1) |
| | | | | | 277.5 | 4.91 | -3 | | | | | (6) |
| | | | | | 301.3 | 2.64 | -2 | | | | | " |
| | | | | | 313.3 | 6.08 | -2 | | | | | (1) |
| | | | | | 338.9 | 1.88 | -1 | 40 | | | | " |
| | | | | | | | $m$ | | | | | |
| | | | | | | 1.0 | 1 | | | | | (6) |
| | | | | | | 8.4 | 0 | | | | | (5) |
| .3 | $D_2 + Br_2 \rightarrow 2\ DBr$ | stat anal(B) | 0.002 - 0.005 | as (.2) | | | $k$ | | | | * | (1) |
| | | | | | 275.8 | 6.79 | -4 | | | | | |
| | | | | | 312.4 | 8.35 | -3 | | | | | |
| | | | | | 317.1 | 1.18 | -2 | | | | | |
| | | | | | 335.7 | 3.21 | -2 | | | | | |
| | | | | | 350.6 | 8.48 | -2 | | | | | |
| | | | | | 366.3 | 1.75 | -1 | | | | | |
| | | | | | 379.5 | 3.67 | -1 | 44 | | | | |
| | | | | | | | $m$ | | | | | |
| | | | | | | 1.0 | 1 | | | | | |
| .4 | $H_2 + I_2 \rightarrow 2\ HI$ | stat anal(B) | 0.02 - 1.00 | $k\,AB$ | | | $k$ | | | | * | (3) |
| | | | | | 283 | 4.45 | -5 | | | | | |
| | | | | | 302 | 1.32 | -4 | | | | | " |
| | | | | | 356 | 2.52 | -3 | | | | | " |
| | | | | | 374 | 5.22 | -3 | | | | | " |
| | | | | | 393 | 1.42 | -2 | | | | | " |
| | | | | | " | 1.56 | -2 | | | | | (13) |

| No. | Reaction | Method | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $H_2 + I_2 \rightarrow 2\ HI$ *(continued)* | stat anal (B) | 0.02 - 1.00 | $k\,AB$ | 410 | 2.46 | -2 | | | | | ([3]) |
| | | | | | 425 | 6.70 | -2 | | | | | ([13]) |
| | | | | | 427 | 6.43 | -2 | | | | | ([3]) |
| | | | | | 443 | 1.40 | -1 | | | | | " |
| | | | | | 508 | 1.34 | 0 | ~ 39 | | | | " |
| .5 | $2\ HI \rightarrow H_2 + I_2$ | stat anal (B) | 0.02 - 1.0 | $k\,A^2$ | 283 | 3.52 | -7 | | | | * | ([3]) |
| | | | | | 300 | 1.18 | -6 | | | | | ([9]) |
| | | | | | 302 | 1.22 | -6 | | | | | ([3]) |
| | | | | | 321 | 3.95 | -6 | | | | | ([9]) |
| | | | | | 356 | 3.02 | -5 | | | | | ([3]) |
| | | | | | 374 | 8.59 | -5 | | | | | " |
| | | | | | 393 | 2.19 | -4 | | | | | " |
| | | | | | " | 2.59 | -4 | | | | | ([13]) |
| | | | | | 410 | 5.12 | -4 | | | | | ([3]) |
| | | | | | 425 | 1.24 | -3 | | | | | ([13]) |
| | | | | | 427 | 1.16 | -3 | | | | | ([3]) |
| | | | | | 443 | 2.50 | -3 | | | | | " |
| | | | | | 508 | 3.95 | -2 | ~ 44 | | | | " |
| | | " | 0.02 - 1.0 | " | 321 | 3.95 | -6 | | | | | ([9]) |
| | | | 2.0 | | " | 4.2 | -6 | | | | | |
| | | | 3.0 | | " | 4.6 | -6 | | | | | |
| | | | 4.0 | | " | 4.8 | -6 | | | | | |
| | | | 6.0 | | " | 5.5 | -6 | | | | | |
| | | | 7.0 | | " | ~ 7 | -6 | | | | | |

| No. | Reaction | Method | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .6 | $D_2 + I_2 \rightarrow 2\ DI$ | stat anal (B) | $(1 - 2) \times 10^{-5}$ | $k$ AB | 393 | 7.95 | -3 | | | | * | ([13]) |
| | | | | | 425 | 3.45 | -2 | | | | | |
| .7 | $2\ DI \rightarrow D_2 + I_2$ | stat anal (B) | $(1 - 2) \times 10^{-5}$ | $k A^2$ | 387 | 1.19 | -4 | | | | * | ([2]) |
| | | | | | 393 | 1.68 | -4 | | | | | ([13]) |
| | | | | | 425 | 7.77 | -4 | | | | | " |
| | | | | | 435 | 1.11 | -3 | | | | | ([2]) |
| | | | | | 446 | 1.83 | -3 | | | | | " |

## COMMENTS

(.1) The data of ([12]) and ([11]) supersede previous work, such as that of Christiansen. For the flow-system reaction ([12]), the second-order $k$ and $E$ were calculated from the original data. These figures can lay claim to no accuracy, and are given in the way of illustration of the order of magnitude. Over longer times, $k$ falls sharply and depends strongly on surface conditions. The simple second-order rate law $k$AB is derivable from the simple Nernst-chain mechanism

$Cl_2 \rightarrow 2\ Cl;\ Cl + H_2 \rightarrow HCl + H;$ etc.

which also accounts for the main features of the photochemical reaction, including in particular the variation in the order in $[Cl_2]$ with the presence or absence of inhibitors. The flow-system thermal reaction ([12]) is inhibited by $O_2$, but in the presence of high amounts of $O_2$ packing accelerates the rate, which is taken to indicate chain generation at the wall. The reaction is thus, essentially, partly heterogeneous, partly homogeneous. The effect of the condition of the reaction vessel wall is illustrated by the static-system reactions ([11]) where the very rate law varies with the nature of the wall. Selected illustrative data are included in the table.

In the uncoated pyrex vessel, the rate is very strongly dependent on the kind of surface; all data listed refer to a constant surface/volume ratio of $\sim 1.2\ cm^{-1}$. For the KCl-coated vessel, $k$ falls strongly with the progress of the reaction (the data included refer to 900, 1800, 3600, 36000 sec). On account of the obvious inconstancy of $k$ in both cases. the rate laws quoted can claim no absolute validity. The law proposed for the reaction in the KCl-coated bulb is derivable from a mechanism involving generation of only Cl atoms at the wall, whereas both Cl and H appear to be generated at the uncoated wall. The chain length is estimated to $\sim 10^4$. The second-order $k$ from the flow experiments, ([12]), when extrapolated down to 284°C with the aid of the temperature coefficient holding between 230 and 250°C, becomes $\sim 2.4 \times 10^{-2}$, i.e. it is not unreasonably close, as far as order of magnitude goes, to the experimental $k$ in the static experiments ([11]) in an uncoated bulb, particularly if it is borne in mind that the second-order flow-system $k$ refers to an early stage of the reaction. The values of $k$ thus appear to be little sensitive to the form of the rate law.

(.2) Data of ([6]) and of ([1]) are combined. The discrepancy

## COMMENTS *(continued)*

between ([6]) and ([1]) is equivalent to almost 10° difference in temperature but it is improbable that the deviations should be due to that factor. The temperature effect is the same in ([6]) and in ([1]). The chain mechanism is now classic, (1) $Br_2 \rightleftarrows 2Br$, (2) $Br + H_2 \longrightarrow HBr + H$, (3) $H + Br_2 \longrightarrow HBr + Br$, (4) $H + HBr \longrightarrow H_2 + Br$, and hence $+ dL/dt = 2\ (k_2 k_3/k_4)\ K^{1/2} AB^{1/2} / [(k_3/k_4) + (L/B)]$. For step (2), $E = 17.7$, $A = 7 \times 10^{10}$. The same mechanism and rate law, with the same value of $m$, render the photochemical reaction. (.3) Mechanism as in (.2). For step (2), $E = 19.9$, $A = 8 \times 10^{10}$. (.4) (.5) Combined data of ([3]) and ([13]) for (.4) and of ([3]), ([9]), and ([13]), for (.5). Data of ([13]) give the temperature variation of the equilibrium constant in agreement with that calculated from the free energy function ([2]), whereas the data of ([3]) do not. The latter data fail to give a linear plot of log $k$ as a function of $1/T$ ([8]), hence $E$ is somewhat uncertain. The reaction may be catalyzed by very extensive pyrex surface ([14]). Loss of $H_2$ by diffusion through quartz cannot be disregarded ([13]). Intensive drying is without effect ([9]). Apparent effect of drying with $P_2O_5$ ([10]) is due to oxidation([4]). For reaction (.5) at higher concentrations, selected points from the 50-point experimental curve of ([9]); the variation of $k$ with the concentration $N$ is expressible by $k = k_o / (1 - Nb)$ where $k_o = 3.95 \times 10^{-6}$ is the rate constant at 0.02 - 1.0 M/l ; the "van der Waals-like" constant $b = 4.7 \times 10^{-2}$ l/M in the range 2 - 4.5 M/l. (.6) (.7) Combined data of ([2]) and ([13]), for reaction (.7), in satisfactory agreement. Data of ([7]) are doubtful on account of the uncertainties involved in the analytical procedure (nonmonochromatic extinction).

## LITERATURE

([1]) Bach, K. F. Bonhoeffer, Moelwyn-Hughes, *ZPC*[B] 1934, **27**, 71. ([2]) J. C. L. Blagg, G. M. Murphy, *JCP* 1936, **4**, 631. ([3]) M. Bodenstein, *ZPC* 1894, **13**, 56; 1897, **22**, 1; 1898, **29**, 295. ([4]) M. Bodenstein, W. Jost, *ACS* 1927, **49**, 1416. ([5]) M. Bodenstein, G. Jung, *ZPC* 1926, **121**, 127. ([6]) M. Bodenstein, S. C. Lind, *ZPC* 1907, **57**, 168. ([7]) Geib and Lendle, *ZPC*[B] 1930, **32**, 463. ([8]) L. S. Kassel, Kinetics of Homogeneous Reactions, Chem. Cat. Co., New York, NY, 1932, p. 148. ([9]) G.B. Kistiakowsky, *ACS* 1928, **50**, 2315. ([10]) B. Lewis, E.K. Rideal, *ACS* 1926, **48**, 2553. ([11]) J.C. Morris, R.N. Pease, *ACS* 1939, **61**, 371 and 396. ([12]) R.N. Pease, *ACS* 1934, **56**, 2385. ([13]) A.H. Taylor, Jr. R.H. Crist, *ACS* 1941, **63**, 1377. ([14]) H.A. Taylor, *JCP* 1924, **28**, 984.

## Nitration of aromatic compounds

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$ | $CH_3NO_2$ | A ~ 0.1 | $HNO_2$ | 0.006 - 0.15 | $k_o = (a + b[HNO_2]^{1/2})^{-1}$ | | | | * | (1) |
| | | | B = 3.0 | | | $a$ | 0 | 1.57 | 5 | | |
| | | | " | | | $b$ | " | 1.88 | 6 | | |
| | | | 3.5 | | | $a$ | " | 1.72 | 5 | | |
| | | | " | | | $b$ | " | 7.00 | 5 | | |
| | | | 4.0 | | | $a$ | " | 8.3 | 4 | | |
| | | | " | | | $b$ | " | 4.75 | 5 | | |
| | | | 4.5 | | | $a$ | " | 5.0 | 4 | | |
| | | | " | | | $b$ | " | 2.70 | 5 | | |
| | | | 5.0 | | | $a$ | " | 1.74 | 4 | | |
| | | | " | | | $b$ | " | 1.73 | 5 | | |
| | | | 5.5 | | | $a$ | " | 1.74 | 4 | | |
| | | | " | | | $b$ | " | 8.80 | 4 | | |
| | | | 6.0 | | | $a$ | " | 7.4 | 3 | | |
| | | | " | | | $b$ | " | 7.03 | 4 | | |
| | | | 6.5 | | | $a$ | " | 5.6 | 3 | | |
| | | | " | | | $b$ | " | 4.85 | 4 | | |
| | | | 7.0 | | | $a$ | " | 3.5 | 3 | | |
| | | | " | | | $b$ | " | 3.30 | 4 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$ *(continued)* | | B = 3.0 | | | *a* | 0 | 1.57 | 5 | | |
| | | | " | | | " | 20 | 2.15 | 4 | | |
| | | | " | | | *b* | 0 | 1.88 | 6 | | |
| | | | " | | | " | 20 | 1.52 | 5 | | |
| | | | B = 5.0 | | | *a* | 0 | 1.74 | 5 | | |
| | | | " | | | " | 10 | 6.0 | 3 | | |
| | | | " | | | *b* | -10 | 5.70 | 4 | | |
| | | | " | | | " | 0 | 1.73 | 4 | | |
| | | | " | | | | 10 | 4.8 | 3 | | |
| | | | B = 4.0 | $HNO_2$ | 0.073 | | 0 | | | | |
| | | | | | | +dL/dt = | | 5.3 | -3 | | |
| .2 | $C_6H_5CH_3 + HNO_3 \longrightarrow CH_3C_6H_4NO_2 + H_2O$ | $CH_3NO_2$ | A ~ 0.1; B = 4.0 | $HNO_2$ | 0.073 | +dL/dt = | | 5.3 | -3 | * | (1) |
| .3 | $C_6H_5C_2H_5 + HNO_3 \longrightarrow C_2H_5C_6H_4NO_2 + H_2O$ | $CH_3NO_2$ | A ~ 0.1; B = 4.0 | $HNO_2$ | 0.073 | +dL/dt = | | 5.3 | -3 | * | (1) |
| .4 | $C_6H_5F + HNO_3 \longrightarrow FC_6H_4NO_2 + H_2O$ | $CH_3NO_2$ | | See Comments | | | | | | * | (1) |
| .5 | $C_6H_5Cl + HNO_3 \longrightarrow ClC_6H_4NO_2 + H_2O$ | $CH_3NO_2$ | | See Comments | | | | | | * | (1) |
| .6 | $C_6H_5Br + HNO_3 \longrightarrow BrC_6H_4NO_2 + H_2O$ | $CH_3NO_2$ | | See Comments | | | | | | * | (1) |
| .7 | $C_6H_5I + HNO_3 \longrightarrow IC_6H_4NO_2 + H_2O$ | $CH_3NO_2$ | | See Comments | | | | | | * | (1) |
| .8 | $C_6H_5NO_2 + HNO_3 \longrightarrow C_6H_4(NO_2)_2 + H_2O$ | $H_2O + H_2SO_4$ % | A = B = | | | *k* AB | | | | * | (5) |
| | | 95.6 | 0.04 0.04 | | | | 5 | 3.7 | -3 | | |
| | | 93.0 | 0.02 0.02 | | | | " | 6.7 | -3 | | |
| | | 90.0 | 0.04 0.04 | | | | " | 9.2 | -3 | | |
| | | 87.5 | 0.02 0.02 | | | | " | 5.5 | -3 | | |
| | | 86.0 | 0.04 0.04 | | | | " | 2.1 | -3 | | |

| No. | Reaction | Solvent | Amount of reactant | | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $C_6H_5NO_2 + HNO_3 \longrightarrow C_6H_4(NO_2)_2 + H_2O$ *(continued)* | 95.6 | 0.02 | 0.02 | | | | 25 | 3.27 | -2 | | |
| | | " | 0.01 | 0.01 | | | | " | 3.67 | -2 | | |
| | | 93.0 | 0.02 | 0.02 | | | | " | 5.30 | -2 | | |
| | | 92.0 | 0.02 | 0.02 | | | | " | 5.70 | -2 | | |
| | | 90.0 | 0.01 | 0.01 | | | | " | 7.00 | -2 | | |
| | | 85.0 | 0.02 | 0.02 | | | | " | 5.20 | -2 | | |
| | | 82.5 | 0.05 | 0.05 | | | | " | 2.2 | -4 | | |
| | | 80.0 | 0.04 | 0.04 | | | | " | 2.3 | -5 | | |
| | | 95.6 | 0.02 | 0.02 | $KHSO_4$ | 0.46 | | " | 3.7 | -2 | | (5) |
| | | 93.0 | 0.02 | 0.02 | " | " | | " | 6.5 | -2 | | |
| | | 92.0 | 0.02 | 0.02 | " | " | | " | 5.5 | -2 | | |
| | | 90.0 | 0.02 | 0.02 | " | " | | " | 6.2 | -2 | | |
| | | 85.0 | 0.02 | 0.02 | " | 0.70 | | " | 2.3 | -3 | | |
| | | 96.5 | 0.02 | 0.02 | | | | 40 | 1.4 | -1 | | |
| | | 93.0 | 0.01 | 0.01 | | | | " | 1.67 | -1 | | |
| | | 91.5 | 0.01 | 0.01 | | | | " | 1.73 | -1 | | |
| | | 90.0 | 0.01 | 0.01 | | | | " | 1.92 | -1 | | |
| | | 87.5 | 0.02 | 0.02 | | | | " | 9.3 | -2 | | |
| | | 85.0 | 0.02 | 0.02 | | | | " | 1.45 | -2 | | |
| | | 82.5 | 0.02 | 0.02 | | | | " | 1.63 | -3 | | |
| .9 | $o - CH_3C_6H_4NO_2 + HNO_3 \longrightarrow CH_3C_6H_4(NO_2)_2 + H_2O$ | $H_2O + H_2SO_4$ 82.5 % | 0.02 | 0.02 | | | $k$AB | 25 | 1.25 | -1 | | (5) |
| .10 | $m - CH_3C_6H_4NO_2 + HNO_3 \longrightarrow CH_3C_6H_4(NO_2)_2 + H_2O$ | $H_2O + H_2SO_4$ 82.5 % | 0.02 | 0.02 | | | $k$AB | 25 | 5.3 | -2 | | (5) |
| .11 | $p - CH_3C_6H_4NO_2 + HNO_3 \longrightarrow CH_3C_6H_4(NO_2)_2 + H_2O$ | $H_2O + H_2SO_4$ 80.0 % | 0.01 | 0.01 | | | $k$AB | 25 | 7.0 | -3 | | (5) |
| | | 82.5 | 0.02 | 0.02 | | | | " | 6.5 | -2 | | |



942151 O—51——21

| No. | Reaction | Solvent | | Amount of reactant | | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .12 | $CH_3C_6H_3(NO_2)_2 + HNO_3 \longrightarrow CH_3C_6H_2(NO_2)_3 + H_2O$ | $H_2O + H_2SO_4$ | 95.6 % | 0.12 | 0.12 | | | $k$AB | 100 | 3.8 | -4 | | (5) |
| | | | 90.0 | " | " | | | | " | 3.5 | -4 | | |
| .13 | $m - (CH_3)_2C_6H_2(NO_2)_2 + HNO_3 \longrightarrow m - (CH_3)_2C_6H(NO_2)_3 + H_2O$ | $H_2O + H_2SO_4$ | 100.1 % | 0.48 | 0.08 | | | $k$AB | 50 | 5.8 | -4 | | (5) |
| | | | " | 0.51 | 1.01 | | | | " | 1.15 | -4 | | |
| | | | 95.6 | 0.02 | 0.02 | | | | " | 7.7 | -4 | | |
| | | | 93.0 | 0.02 | 0.40 | | | | " | 3.0 | -3 | | |
| | | | " | 0.09 | 0.09 | | | | " | 2.7 | -3 | | |
| | | | 90.0 | 0.02 | 0.40 | | | | " | 1.4 | -3 | | |
| .14 | $(CH_3)_3CH(NO_2)_2 + HNO_3 \longrightarrow (CH_3)_3C(NO_2)_3 + H_2O$ | $H_2O + H_2SO_4$ | 95.6 % | 0.02 | 0.02 | | | $k$AB | 25 | 1.03 | -2 | | (5) |
| | | | 91.5 | 0.01 | 0.01 | | | | " | 1.8 | -2 | | |
| | | | 90.0 | 0.02 | 0.02 | | | | " | 2.3 | -2 | | |
| | | | 88.5 | 0.01 | 0.01 | | | | " | 1.23 | -2 | | |
| | | | 85.0 | 0.01 | 0.01 | | | | " | 2.7 | -3 | | |
| .15 | $C_6H_5CH_2COOH + HNO_3 \longrightarrow C_6H_4(NO_2)CH_2COOH + H_2O$ | $H_2O + H_2SO_4$ | 90.0 % | 0.02 | 0.02 | | | $k$AB | 25 | 6.5 | -2 | | (5) |

## COMMENTS

(.1) (.2) (.3) With a large excess of $HNO_3$, the reaction in organic solvents ($CH_3NO_2$, dioxane, $CH_3COOH$, $CH_3CN$, $(CH_3CO)_2O$) is zero-order in A; the zero-order rate constant $k_o$ is a function of $[HNO_2]$, as given in the table. Empirically, the parameters $a$ and $b$, at 0°C, are functions of $B = [HNO_3]$ of the form $a = 8.4 \times 10^9 B^{-6}(27 - B)^{-1}$ and $b = 11.3 \times 10^9 B^{-5}(27 - B)^{-1}$. The rates of reactions (.1) (.2) (.3) are practically the same. Strong acids ($H_2SO_4$) accelerate the rate; $NO_3^-$ ion retards it. Discussion of the data (2) (3) (4) leads to the conclusion

## COMMENTS *(continued)*

that the rate determining step is $2\ HNO_3 \rightarrow H_2NO_3^+ + NO_3^-$, ($H_2NO_3^+ \rightleftarrows H_2O + NO_2^+$), with the nitronium ion $NO_2^+$ the effective nitrating agent. In reactions (.1) (.2) (.3), the reaction of $NO_2^+$ with A is rapid as compared with the rate-determining step, hence the zero-order in A.

**(.4) (.5) (.6) (.7)** The order of these reactions is between 0 and 1, as the rates of the reactions between A and $NO_2^+$ are comparable with the rate of the rate determining step $2\ HNO_3 \rightarrow NO_3^- + H_2NO_3^+$ ($\rightleftarrows H_2O + NO_2^+$).

**(.8) - (.15)** In $H_2O + H_2SO_4$, the nitration proceeds over $HNO_3 + H_2SO_4 \rightleftarrows HSO_4^- + H_2NO_3^+$; $H_2NO_3^+ + H_2SO_4 \rightleftarrows HSO_4^- + H_3O^+ + NO_2^+$.

## LITERATURE

(1) G.A.Benford, C.K.Ingold, *CSL* **1938**, 829. (2) G.A.Benford, C.A.Bunton, E.S.Halberstadt, E.D.Hughes, C.K.Ingold, G.G.Minkoff, R.T.Reed, *Nature* 1945, **156**, 688. (3) C.A.Bunton, E.D.Hughes, G.J.Minkoff, R.T.Reed, *Nature* 1946, **158**, 514. (4) C.A.Bunton, E.D.Hughes, G.J.Minkoff, R.T.Reed, *Nature* 1946, **158**, 514. (5) F.H.Westheimer, M.S.Kharasch, *ACS* 1946, **68**, 1871.

## Sulfonation of aromatic compounds

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .1 | $p - CH_3C_6H_4NO_2 + H_2SO_4 \rightarrow 1 - CH_3 - 2 - SO_3H - C_6H_3 - 4 - NO_2$ | $H_2SO_4$ 97.6 % + $SO_3$ 2.4 % | A = 0.1 | $k$A | 25 | 5 | -5 | (1) |
| | | | | | 35 | 1 | -4 | |
| | | | | | 45 | 2.5 | -4 | |
| | | $H_2SO_4$ 100 % | " | " | 25 | 7 | -6 | " |

## COMMENTS

The values of $k$ are *initial*. $H_2O$ formed in the course of the reaction acts as inhibitor, and $k$ falls with time, particularly in the absence of initial $SO_3$.

Sulfonation of $C_6H_6$, $CH_3C_6H_5$, $C_{10}H_8$, $C_6H_5OH$, $C_6H_5C_6H_5$, etc., with $H_2SO_4$ in the presence of $BF_3$ (catalyst): data of times of completion, see (2).

## LITERATURE

(1) H.Martinsen, *ZPC* 1908, 62, 713. (2) R.J.Thomas, N.F.Anzilotti, G.F.Hennion, *IEC* 1940, 32, 408.

# EXCHANGE

## of H for halogen on aliphatic C.

*Liquid phase*

Reaction type $RH + X_2 \rightarrow RX + HX$

(A) (B) (L) (M)

Rate measured $-dB/dt$

Amounts are in M/l.

Rates are in M/l per sec.

Where there may be doubt about the position of the substitution, the H exchanged is printed in bold-face type.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **Aliphatic-aliphatic Ketone** | | | | | | | | | | |
| .1 | $CH_3COCH_3 + Cl_2$ | $H_2O$ | A = 0.068; B = 0.0014 | NaOH | 0.035 | $kA$ | 0 | 1.03 | -3 | | | | | (1) |
| | | | 0.223 | | " | | 0 | 1.25 | -3 | | | | | |
| | | | 0.0015 | | 0.070 | | 0 | 1.54 | -3 | | | | | |
| .2 | $CH_3COCH_3 + Br_2$ | A + 9.1 vol % $H_2O$ | $10^3B = 1 - 3$ | HCl | 0.0108 | $-dB/dt$ | -20.6 | 3.8 | -8 | | | | * | (3) |
| | | | | | 0.0427 | | " | 2.04 | -7 | | | | | |
| | | | | | 0.0744 | | " | 4.3 | -7 | | | | | |
| | | | | | 0.117 | | " | 8.5 | -7 | | | | | |
| | | | | | 0.145 | | " | 1.14 | -6 | | | | | |
| | | A + 9.1 vol % $H_2O$ | $10^3B = 1 - 3$ | HBr | 0.0375 | $-dB/dt$ | -20.6 | 1.07 | -7 | | | | * | (3) |
| | | | | | 0.045 | | " | 1.4 | -7 | | | | | |
| | | | | | 0.0818 | | " | 2.1 | -7 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3COCH_3 + Br_2$ *(continued)* | | | HBr | 0.0251 | $-dB/dt$ | -11.3 | 3.1 | -7 | | | | | ([3]) |
| | | | | | 0.045 | | " | 5.75 | -7 | | | | | |
| | | | | " | 0.0118 | " | 0.0 | 7.75 | -7 | | | | | " |
| | | | | | 0.045 | | " | 3.8 | -6 | | | | | |
| | | | | | 0.0624 | | " | 4.5 | -6 | | | | | |
| | | $H_2O$ | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 5 | 2.55 | -7 | | | | * | ([4]) |
| | | | | | | | 15 | 9.20 | -7 | | | | | |
| | | | | | | | 25 | 3.07 | -6 | | | | | |
| | | | | | | | 35 | 1.03 | -5 | 20.3 | | | | |
| | | Ac 25 | " | " | " | " | 15 | 1.15 | -6 | | | | | " |
| | | | | | | | 25 | 3.70 | -6 | | | | | |
| | | | | | | | 35 | 1.15 | -5 | 20.0 | | | | |
| | | Ac 50 | " | " | " | " | 0 | 2.28 | -7 | | | | | " |
| | | | | | | | 15 | 1.54 | -6 | | | | | |
| | | | | | | | 25 | 4.98 | -6 | 19.7 | | | | |
| | | Ac 75 | " | " | " | " | 0 | 4.53 | -7 | | | | | " |
| | | | | | | | 15 | 3.27 | -6 | | | | | |
| | | | | | | | 25 | 1.06 | -5 | 20.1 | | | | |
| | | $H_2O$ | " | $CH_3COO^-$ | 0.147 | " | 35 | 1.78 | -7 | | | | * | " |
| | | | | | | | 45 | 5.15 | -7 | | | | | |
| | | | | | | | 55 | 1.41 | -6 | 20.7 | | | | |
| | | Ac 25 | " | " | " | " | 35 | 3.08 | -7 | | | | | " |
| | | | | | | | 45 | 8.65 | -7 | | | | | |
| | | | | | | | 55 | 2.23 | -6 | 19.0 | | | | |
| | | Ac 50 | " | " | " | " | 35 | 4.67 | -7 | | | | | " |
| | | | | | | | 45 | 1.28 | -6 | | | | | |
| | | | | | | | 55 | 3.37 | -6 | 19.4 | | | | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .2 | $CH_3COCH_3 + Br_2$ *(continued)* | Ac 75 | A = 0.1 | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 35 | 5.83 | -7 | | | | | (4) |
| | | | | | | | 45 | 1.53 | -6 | | | | | |
| | | | | | | | 55 | 3.77 | -6 | 18.5 | | | | |
| | | Ac 90 | " | " | " | " | 35 | 5.63 | -7 | | | | | " |
| | | | | | | | 45 | 1.50 | -6 | | | | | |
| | | | | | | | 55 | 3.62 | -6 | 19.3 | | | | |
| | | A + 9.1 vol % $H_2O$ | $10^3B = 1 - 3$, $M \sim 0.01 - 0.1$ | $kM$; $k'M(1 + 1.5\ M)$ | | | | | | | | | | (3) |
| | | | | | | $k$ | -20.6 | 2.8 | -6 | | | | | |
| | | | | | | | 0.0 | 7.0 | -5 | | | | | |
| | | | | | | $k'$ | -40.0 | 6.7 | -6 | | | | | " |
| | | | | | | | -20.6 | 1.76 | -6 | | | | | |
| | | | | | | | 0.0 | 3.60 | -5 | | | | | |
| | | | | | | | +10.1 | 1.33 | -4 | 19.9 | 4.9 | 11 | | |
| | | $H_2O$ | A ~ 0.5; B ~ 0.003 | HCl | ~ 0.1 - 0.3 | $kA[H^+]$ | 25 | 2.8 | -5 | | | | | (19) |
| | | $D_2O$ | " | DCl | " | " | " | 5.9 | -5 | | | | | " |
| .3 | $CD_3COCD_3 + Br_2$ | $H_2O$ | A ~ 0.5, B ~ 0.03 | HCl | 0.1 - 0.3 | $kA[H^+]$ | 25 | 3.7 | -6 | | | | | (17) |
| | | $D_2O$ | " | DCl | " | $kA[D^+]$ | 25 | 7.7 | -6 | | | | | " |
| .4 | $CH_3COCH_3 + I_2$ | $H_2O$ | A = 0.028, $10^3B = 4 - 5$ | HCl | $(2 - 8)10^{-5}$ | $kA[H^+]$ | 25 | 2.90 | -5 | | | | * | (8) |
| | | " | " | " | 0.01 - 0.1 | $kA[H^+]$ | 25 | 2.83 | -5 | See Supplementary Table | | | * | (9) |
| | | | | | 0.2 | | " | 2.91 | -5 | | | | | |
| | | | | | 0.5 | | " | 2.99 | -5 | | | | | |
| | | | | | 1.0 | | " | 3.05 | -5 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $CH_3COCH_3 + I_2$ *(continued)* | $H_2O$ | 0.03 - 0.10 | HCl | 0.03 - 0.11 | $kA[H^+]$ | 0 | 1.15 | -6 | | | | * | (21) |
| | | | | | | | 25 | 2.86 | -5 | | | | | |
| | | | | | | | 27 | 3.60 | -5 | | | | | |
| | | | | | | | 35 | 8.80 | -5 | 20.6 | | | | |
| | | | " | $HNO_3$ | " | " | 25 | 2.87 | -5 | | | | | " |
| | | | " | $H_2SO_4$ | " | " | 25 | 2.60 | -5 | | | | | " |
| | | | | " | 0.05 - 0.07 | " | 20 | 1.37 | -5 | | | | * | (20) |
| | | | | | | | 25 | 2.40 | -5 | | | | | |
| .5 | $C_2H_5CH(CH_3)COCH_3 + I_2$ | $CH_3COOH$ | A = 0.9 | $HNO_3$ | 1.19 | $kA$ | 15 | 9.6 | -3 | | | | | (2) |
| | | | | | | | 25 | 2.3 | -2 | | | | | |
| | | | | | | | 38.7 | 7.6 | -2 | | | | | |
| .6 | $C_2H_5CH(CH_3)COC_2H_5 + I_2$ | $CH_3COOH$ | A = 0.9 | $HNO_3$ | 1.19 | $kA$ | 15 | 5.5 | -3 | | | | | (2) |
| | | | | | | | 25 | 1.42 | -2 | | | | | |
| | | | | | | | 38.7 | 7.58 | -2 | | | | | |
| .7 | $C_2H_5CH(CH_3)COCH_2C_6H_5 + I_2$ | $CH_3COOH$ | A = 0.9 | $HNO_3$ | 1.19 | $kA$ | 24.5 | 5.1 | -3 | | | | | (2) |
| | | | | | | | 38.7 | 2.1 | -3 | | | | | |
| | **Keto-Ketones** | | | | | | | | | | | | | |
| .8 | $CH_3COCH_2COCH_3 + Br_2$ | $H_2O$ | A = 0.0004<br>B = 0.025 | | | $kA$ | 25 | 1.72 | -2 | | | | * | (2a) |
| | | " | " | X = | | $kA[X]$ | | | | | | | | |
| | | | | $CH_2ClCOO^-$ | | | 25 | 3.3 | -1 | | | | * | " |
| | | | | $m\text{-}NO_2C_6H_4COO^-$ | | | " | 7.5 | -1 | | | | | |
| | | | | $CH_2OHCOO^-$ | | | " | 8.3 | -1 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $CH_3COCH_2COCH_3 + Br_2$ *(continued)* | | | X = | | | | | | | | | | |
| | | | | $CH_2ClCH_2COO^-$ | | | 25 | 1.28 | 0 | | | | | |
| | | | | $C_6H_5CH_2COO^-$ | | | " | 1.50 | 0 | | | | | |
| | | | | $C_6H_5COO^-$ | | | " | 1.60 | 0 | | | | | |
| | | | | $CH_3COO^-$ | | | " | 2.66 | 0 | | | | | |
| | | | | $C_6H_5CH_2CH_2COO^-$ | | | " | 3.00 | 0 | | | | | |
| | | | | $C_2H_5COO^-$ | | | " | 3.17 | 0 | | | | | |
| | | | | $(CH_3)_3CCOO^-$ | | | " | 3.66 | 0 | | | | | |
| | | | | $(CH_3)_2CHCH_2COO^-$ | | | " | 4.17 | 0 | | | | | |
| 9 | $CH_3COCHBrCOCH_3 + Br_2$ | $H_2O$ | A = 0.0004<br>B = 0.025 | | | $kA$ | 25 | 2.32 | -2 | | | | * | ([2a]) |
| | | " | " | X = | | $kA[X]$ | | | | | | | | |
| | | | | $CH_2ClCOO^-$ | | | 25 | 6.01 | -1 | | | | * | " |
| | | | | $m\text{-}NO_2C_6H_4COO^-$ | | | " | 3.25 | 0 | | | | | |
| | | | | $CH_2OHCOO^-$ | | | " | 1.66 | 0 | | | | | |
| | | | | $CH_2ClCH_2COO^-$ | | | " | 3.75 | 0 | | | | | |
| | | | | $C_6H_5CH_2COO^-$ | | | " | 6.66 | 0 | | | | | |
| | | | | $C_6H_5COO^-$ | | | " | 4.66 | 0 | | | | | |
| | | | | $CH_3COO^-$ | | | " | 4.50 | 0 | | | | | |
| | | | | $C_6H_5CH_2CH_2COO^-$ | | | " | 1.30 | +1 | | | | | |
| | | | | $C_2H_5COO^-$ | | | " | 6.17 | 0 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .9 | $CH_3COCHBrCOCH_3 + Br_2$ *(continued)* | | | $(CH_3)_3CCOO^-$ | | | 25 | 1.20 | +1 | | | | | |
| | | | | $(CH_3)_2CHCH_2COO^-$ | | | " | 1.00 | +1 | | | | | |
| .10 | $CH_3COCH_2COOC_2H_5 + Br_2$ | $H_2O$ | A = 0.0004<br>B = 0.025 | | | $kA$ | 25 | 1.20 | -3 | | | | * | ([2a]) |
| | | " | " | X = | | $kA[X]$ | | | | | | | | |
| | | | | $CHCl_2COO^-$ | | | 25 | 3.80 | -2 | | | | * | " |
| | | | | $m$-$NO_2C_6H_4COO^-$ | | | " | 1.08 | -1 | | | | | |
| | | | | $CH_2OHCOO^-$ | | | " | 1.33 | -1 | | | | | |
| | | | | $C_6H_5COO^-$ | | | " | 2.5 | -1 | | | | | |
| | | | | $C_6H_5CH_2COO^-$ | | | " | 3.3 | -1 | | | | | |
| | | | | $CH_3COO^-$ | | | " | 4.8 | -1 | | | | | |
| | | | | $C_2H_5COO^-$ | | | " | 5.3 | -1 | | | | | |
| | | | | $C_6H_5CH_2CH_2COO^-$ | | | " | 5.7 | -1 | | | | | |
| | | | | $(CH_3)_2CHCOO^-$ | | | " | 6.5 | -1 | | | | | |
| | | | | $(CH_3)_2CHCH_2COO^-$ | | | " | 6.8 | -1 | | | | | |
| | | | | $(CH_3)_3CCOO^-$ | | | " | 7.2 | -1 | | | | | |
| | | | | $n$-$C_4H_9COO^-$ | | | " | 7.3 | -1 | | | | | |
| .11 | $C_6H_5COCH_2COCH_3 + Br_2$ | $H_2O$ | A = 0.0004<br>B = 0.025 | | | $kA$ | 25 | 1.83 | -4 | | | | * | ([2a]) |
| | | " | " | X = | | $kA[X]$ | | | | | | | | |
| | | | | $CH_2ClCOO^-$ | | | 25 | 6.10 | -3 | | | | * | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $C_6H_5COCH_2COCH_3 + Br_2$ *(continued)* | | | $CH_2OHCOO^-$ | | | 25 | 2.08 | -2 | | | | | |
| | | | | $CH_2ClCH_2COO^-$ | | | " | 3.94 | -2 | | | | | |
| | | | | $m\text{-}NO_2C_6H_4COO^-$ | | | " | 4.00 | -2 | | | | | |
| | | | | $C_6H_5COO^-$ | | | " | 4.06 | -2 | | | | | |
| | | | | $C_6H_5CH_2COO^-$ | | | " | 5.62 | -2 | | | | | |
| | | | | $CH_3COO^-$ | | | " | 6.17 | -2 | | | | | |
| | | | | $(CH_3)_3CCOO^-$ | | | " | 1.11 | -1 | | | | | |
| | | | | $(CH_3)_2CHCH_2COO^-$ | | | " | 1.17 | -1 | | | | | |
| | | | | $C_6H_5CH_2CH_2COO^-$ | | | " | 1.61 | -1 | | | | | |
| .12 | $C_6H_5COCHBrCOCH_3 + Br_2$ | $H_2O$ | A = 0.0004<br>B = 0.025 | | | $kA$ | 25 | 5.5 | -3 | | | | * | ([2a]) |
| | | " | " | X = | | $kA[X]$ | | | | | | | | |
| | | | | $CH_2ClCOO^-$ | | | 25 | 1.80 | -1 | | | | | |
| | | | | $CH_2OHCOO^-$ | | | " | 6.25 | -1 | | | | | |
| | | | | $CH_2ClCH_2COO^-$ | | | " | 1.18 | 0 | | | | | |
| | | | | $m\text{-}NO_2C_6H_4COO^-$ | | | " | 1.20 | 0 | | | | | |
| | | | | $C_6H_5COO^-$ | | | " | 1.22 | 0 | | | | | |
| | | | | $C_6H_5CH_2COO^-$ | | | " | 1.73 | 0 | | | | | |
| | | | | $CH_3COO^-$ | | | " | 1.85 | 0 | | | | | |
| | | | | $(CH_3)_3CCOO^-$ | | | " | 3.33 | 0 | | | | | |
| | | | | $(CH_3)_2CHCH_2COO^-$ | | | " | 3.50 | 0 | | | | | |
| | | | | $C_6H_5CH_2CH_2COO^-$ | | | " | 4.83 | 0 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Aromatic-aliphatic Ketone** | | | | | | | | | | | | | |
| .13 | $CH_3COC_6H_5 + Br_2$ | Ac 25 | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 25 | 1.43 | -6 | | | | * | (4) |
| | | | | | | | 35 | 4.27 | -6 | | | | | |
| | | | | | | | 45 | 1.15 | -5 | 19.4 | | | | |
| | | Ac 50 | " | " | " | " | 25 | 1.83 | -6 | | | | | " |
| | | | | | | | 35 | 5.37 | -6 | | | | | |
| | | | | | | | 45 | 1.47 | -5 | 19.2 | | | | |
| | | Ac 75 | " | " | " | " | 15 | 1.25 | -6 | | | | (4) (13) (11) | |
| | | | | | | | 25 | 4.05 | -6 | | | | | |
| | | | | | | | 35 | 1.25 | -5 | | | | | |
| | | | | | | | 45 | 3.60 | -5 | 20.2 | | | | |
| | | Ac 90 | " | " | " | " | 5 | 2.10 | -6 | | | | | (4) |
| | | | | | | | 15 | 7.43 | -6 | | | | | |
| | | | | | | | 25 | 2.40 | -5 | 19.8 | | | | |
| | | Ac 50 | " | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 35 | 2.57 | -7 | | | | | " |
| | | | | | | | 45 | 7.17 | -7 | | | | | |
| | | | | | | | 55 | 1.98 | -6 | 20.3 | | | | |
| | | Ac 75 | " | " | " | " | 35 | 2.90 | -7 | | | | | " |
| | | | | | | | 45 | 7.38 | -7 | | | | | |
| | | | | | | | 55 | 1.87 | -6 | 18.4 | | | | |
| | | Ac 90 | " | " | " | " | 35 | 2.62 | -7 | | | | | " |
| | | | | | | | 45 | 7.05 | -7 | | | | | |
| | | | | | | | 55 | 1.85 | -6 | 19.3 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .13 | $CH_3COC_6H_5 + Br_2$ *(continued)* | Ac 75 | A = 0.1 | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 45 | 8.7 | -7 | | | | * | (12) |
| | | | | | | | 55 | 2.08 | -6 | | | | | |
| | | | | | | | 65 | 5.50 | -6 | 19.4 | | | | |
| .14 | $CH_3CO(m\text{-}C_6H_4CH_3) + Br_2$ | Ac 75 | " | HCl | 0.5 | " | 15 | 1.49 | -6 | | | | * | (13) |
| | | | | | | | 25 | 4.95 | -6 | | | | | |
| | | | | | | | 35 | 1.39 | -5 | 20.0 | | | | |
| .15 | $CH_3CO(m\text{-}C_6H_4NO_2) + Br_2$ | Ac 75 | " | " | " | " | 15 | 5.0 | -7 | | | | * | (13) |
| | | | | | | | 25 | 1.65 | -6 | | | | | |
| | | | | | | | 35 | 5.40 | -6 | | | | | |
| | | | | | | | 45 | 1.59 | -5 | 21.0 | | | | |
| .16 | $CH_3CO(p\text{-}C_6H_4NO_2) + Br_2$ | Ac 75 | " | " | " | " | 15 | 6.2 | -7 | | | | * | (13) |
| | | | | | | | 25 | 1.97 | -6 | | | | | |
| | | | | | | | 35 | 6.30 | -6 | | | | | |
| | | | | | | | 45 | 1.90 | -5 | 21.0 | | | | |
| .17 | $CH_3CO(m\text{-}C_6H_4F) + Br_2$ | Ac 75 | " | " | " | " | 25 | 2.75 | -6 | | | | * | (13) |
| | | | | | | | 35 | 7.10 | -6 | | | | | |
| | | | | | | | 45 | 2.57 | -5 | 20.7 | | | | |
| .18 | $CH_3CO(p\text{-}C_6H_4F) + Br_2$ | Ac 75 | " | " | " | " | 25 | 2.99 | -6 | | | | * | (13) |
| | | | | | | | 35 | 9.60 | -6 | | | | | |
| | | | | | | | 45 | 2.72 | -5 | 20.5 | | | | |
| .19 | $CH_3CO(m\text{-}C_6H_4Cl) + Br_2$ | Ac 75 | " | " | " | " | 15 | 1.22 | -6 | | | | * | (13) |
| | | | | | | | 25 | 2.44 | -6 | | | | | |
| | | | | | | | 35 | 7.90 | -6 | | | | | |
| | | | | | | | 45 | 2.31 | -5 | 20.8 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .20 | $CH_3CO(m\text{-}C_6H_4Br) + Br_2$ | Ac 75 | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 15 | 1.23 | -6 | | | | * | (13) |
| | | | | | | | 25 | 2.29 | -6 | | | | | |
| | | | | | | | 35 | 8.00 | -6 | | | | | |
| | | | | | | | 45 | 2.34 | -5 | 20.8 | | | | |
| .21 | $CH_3CO(p\text{-}C_6H_4Br) + Br_2$ | Ac 75 | " | " | " | " | 15 | 9.7 | -7 | | | | * | (13) |
| | | | | | | | 25 | 3.19 | -6 | | | | | |
| | | | | | | | 35 | 9.50 | -6 | | | | | |
| | | | | | | | 45 | 2.90 | -5 | 20.4 | | | | |
| .22 | $CH_3CO(m\text{-}C_6H_4I) + Br_2$ | Ac 75 | " | " | " | " | 15 | 1.24 | -6 | | | | * | (13) |
| | | | | | | | 25 | 2.50 | -6 | | | | | |
| | | | | | | | 35 | 1.81 | -5 | | | | | |
| | | | | | | | 45 | 2.35 | -5 | 20.7 | | | | |
| .23 | $CH_3CO(p\text{-}C_6H_4I) + Br_2$ | Ac 75 | " | " | " | " | 25 | 3.25 | -6 | | | | * | (13) |
| | | | | | | | 35 | 1.00 | -5 | | | | | |
| | | | | | | | 45 | 2.93 | -5 | 20.4 | | | | |
| .24 | $CH_3COC_6H_5 + I_2$ | $H_2O$ | $10^3A = 5 - 8$ | $HClO_4$ | 0.021 | $kA$ | 25 | 2.60 | -6 | | | | | (14) (15) |
| | | | $10^5B = 7 - 50$ | | 0.716 | | " | 9.51 | -6 | | | | | |
| | | | | | 1.39 | | " | 1.84 | -5 | | | | | |
| | | | | | 3.02 | | " | 6.56 | -5 | | | | | |
| | | " | " | $H_2SO_4$ | 0.053 | " | 25 | 1.10 | -6 | | | | | " |
| | | | | | 0.1618 | | " | 3.10 | -6 | | | | | |
| | | | | | 0.530 | | " | 1.25 | -5 | | | | | |
| | | | | | 1.94 | | " | 8.70 | -5 | | | | | |
| | | | | | 4.03 | | " | 4.30 | -4 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .25 | $CH_3CO(p\text{-}C_6H_4CH_3) + I_2$ | $H_2O$ | $10^3A = 5 - 8$<br>$10^5B = 7 - 50$ | $HClO_4$ | 1.388 | $kA$ | 25 | 2.17 | -5 | | | | | (14) (15) |
| .26 | $CH_3CO(2,4,6\text{-}C_6H_2(CH_3)_3) + I_2$ | $H_2O$ | $10^3A = 5 - 8$<br>$10^5B = 7 - 50$ | $HClO_4$ | 1.388 | $kA$ | 25 | 2.71 | -5 | | | | | (14) (15) |
| .27 | $CH_3CO(p\text{-}C_6H_4Br) + I_2$ | $H_2O$ | $10^3A = 5 - 8$<br>$10^5B = 7 - 50$ | $HClO_4$ | 1.388 | $kA$ | 25 | 1.42 | -5 | | | | | (14) (15) |
| .28 | $CH_3CH_2COC_6H_5 + Br_2$ | Ac 75 | $A = 0.1$ | HCl | 0.5 | $-dA/dt$ | 25 | 1.90 | -6 | | | | * | (11) |
| | | | | | | | 35 | 5.35 | -6 | | | | | |
| | | | | | | | 45 | 1.87 | -5 | 22.1 | | | | |
| | | Ac 75 | $A = 0.1$ | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 45 | 1.33 | -7 | | | | * | (12) |
| | | | | | | | 55 | 3.70 | -7 | | | | | |
| | | | | | | | 65 | 9.40 | -7 | 19.9 | | | | |
| .29 | $CH_3CH_2COC_6H_5 + I_2$ | $H_2O$ | $10^3A = 5 - 8$<br>$10^5B = 7 - 50$ | $HClO_4$ | 1.388 | $kA$ | 25 | 8.56 | -6 | | | | | (14) (15) |
| .30 | $C_2H_5CH_2COC_6H_5 + Br_2$ | Ac 75 | $A = 0.1$ | HCl | 0.5 | $-dA/dt$ | 25 | 1.20 | -6 | | | | * | (11) |
| | | | | | | | 35 | 4.07 | -6 | | | | | |
| | | | | | | | 45 | 1.29 | -5 | | | | | |
| | | Ac 75 | $A = 0.1$ | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 45 | 1.04 | -7 | | | | * | (12) |
| | | | | | | | 55 | 2.90 | -7 | | | | | |
| | | | | | | | 65 | 7.30 | -7 | 20.2 | | | | |
| .31 | $C_2H_5CH_2COC_6H_5 + I_2$ | $H_2O$ | $10^3A = 5 - 8$<br>$10^5B = 7 - 50$ | $HClO_4$ | 1.388 | $kA$ | 25 | 6.97 | -6 | | | | | (14) (15) |



942151 O—51——22.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .32 | $(CH_3)_2CHCOC_6H_5 + Br_2$ | Ac 75 | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 25 | 3.6 | -7 | | | | * | (11) |
| | | | | | | | 35 | 1.22 | -6 | | | | | |
| | | | | | | | 45 | 3.85 | -6 | 22.1 | | | | |
| | | Ac 75 | A = 0.1 | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 45 | 2.6 | -8 | | | | * | (12) |
| | | | | | | | 55 | 7.4 | -8 | | | | | |
| | | | | | | | 65 | 2.0 | -7 | 20.9 | | | | |
| .33 | $(CH_3)_2CHCOC_6H_5 + I_2$ | $H_2O$ | $10^3A = 5 - 8$ $10^5B = 7 - 50$ | $HClO_4$ | 1.388 | $kA$ | 25 | 3.73 | -7 | | | | | (14) (15) |
| .34 | $C_3H_7CH_2COC_6H_5 + Br_2$ | Ac 75 | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 25 | 1.42 | -6 | | | | * | (11) |
| | | | | | | | 35 | 4.73 | -6 | | | | | |
| | | | | | | | 45 | 1.46 | -5 | | | | | |
| | | Ac 75 | A = 0.1 | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 45 | 1.17 | -7 | | | | * | (12) |
| | | | | | | | 55 | 3.10 | -7 | | | | | |
| | | | | | | | 65 | 8.0 | -7 | 20.1 | | | | |
| .35 | $(CH_3)_2CHCH_2COC_6H_5 + Br_2$ | Ac 75 | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 25 | 5.6 | -7 | | | | * | (12) |
| | | | | | | | 35 | 1.87 | -6 | | | | | |
| | | | | | | | 45 | 5.80 | -6 | 21.7 | | | | |
| | | Ac 75 | A = 0.1 | $CH_3COO^-$ | 0.147 | $-dA/dt$ | 45 | 5.1 | -8 | | | | * | (12) |
| | | | | | | | 55 | 1.42 | -7 | | | | | |
| | | | | | | | 65 | 3.70 | -7 | 20.5 | | | | |
| .36 | $C_4H_9CH_2COC_6H_5 + Br_2$ | Ac 75 | A = 0.1 | HCl | 0.5 | $-dA/dt$ | 25 | 1.37 | -6 | | | | * | (11) |
| | | | | | | | 35 | 4.45 | -6 | | | | | |
| | | | | | | | 45 | 1.37 | -5 | 21.4 | | | | |
| .37 | $C_2H_5CH(CH_3)COC_6H_5 + I_2$ | $CH_3COOH$ | A = 0.9 | $HNO_3$ | 1.19 | $kA$ | 36.7 | 5.0 | -4 | | | | | (2) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Nitro-compounds** | | | | | | | | | | | | | |
| .38 | $CH_3NO_2 + 3\ Br_2 \rightarrow CBr_3NO_2 + 3\ HBr$ | $H_2O$ | | HBr | 1 | $k$ A | 35.0 | 1.5 | -7 | | | | | (16) |
| | | | | | | | 49.9 | 8.1 | -7 | | | | | |
| | | | | | | | 59.9 | 2.3 | -6 | | | | | |
| | | | | | | | 69.8 | 6.0 | -7 | | | | | |
| | | | | HCl | 1 | " | 69.8 | 6.5 | -7 | | | | | " |
| | | $H_2O$, $D_2O$ | A = 0.15 - 0.70<br>B ~ 0.03 | $H_2SO_4$<br>$CH_3COO^-$<br>$CH_2ClCOO^-$ | See | $CH_3NO_2 + \begin{cases} H_2O(D_2O) \\ CH_3COO^- \\ CH_2ClCOO^- \end{cases} \rightarrow CH_2{:}NO_2^- + \begin{cases} H_3O^+(HD_2O^+) \\ CH_3COOH \\ CH_2ClCOOH \end{cases}$ 402.450. | | | | | | | * | (18)<br>(17)<br>(16) |
| .39 | $CD_3NO_2 + 3\ Br_2 \rightarrow CBr_3NO_2 + 3\ DBr$ | $H_2O$, $D_2O$ | A = 0.15 - 0.70<br>B ~ 0.03 | $H_2SO_4$<br>$CH_3COO^-$<br>$CH_2ClCOO^-$ | See | $CD_3NO_2 + \begin{cases} H_2O(D_2O) \\ CH_3COO^- \\ CH_2ClCOO^- \end{cases} \rightarrow CD_2{:}NO_2^- + \begin{cases} H_2DO^+(D_3O^+) \\ CH_3COOD \\ CH_2ClCOOD \end{cases}$ 402.450. | | | | | | | * | (18) |
| .40 | $CH_2BrNO_2 + 2\ Br_2 \rightarrow CBr_3NO_2 + 2\ HBr$ | $H_2O$ | A = 0.01 - 0.04<br>B = 0.02 - 0.04 | HBr | 1 | $k$ A | 35.0 | 2.0 | -3 | | | | | (16) |
| .41 | $CH_2BrNO_2 + Br_2 \rightarrow CHBr_2NO_2 + HBr$ | $H_2O$ | A = 0.01 - 0.04<br>B = 0.02 - 0.04 | HBr | 1 | $k$ A | 35.0 | 3.9 | -5 | | | | * | (16) |
| .42 | $CHBr_2NO_2 + Br_2 \rightarrow CBr_3NO_2 + HBr$ | $H_2O$ | A = 0.01 - 0.02 | HBr | 1 | $k$ A | 5.0 | 6.1 | -5 | | | | * | (16) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .42 | $CHBr_2NO_2 + Br_2 \rightarrow CBr_3NO_2 + HBr$ *(continued)* | | B = 0.01 - 0.04 | | | | 10.0 | 1.16 | -4 | | | | | |
| | | | | | | | 14.9 | 2.16 | -4 | | | | | |
| | | | | | | | 35.0 | (2.0) | -3 | | | | | |
| .43 | $(CH_3)_2CHNO_2 + Br_2$ | $H_2O$ | | HBr | 1 | $kA$ | 59.9 | 5.0 | -7 | | | | | [16] |

## SUPPLEMENTARY TABLE

(.4) $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ ([10])([6])([9])([7])

*Solvent* $H_2O$; A = 0.272; B = 0.005; Temperature 25°C.

Data of $-10^6$ (dA/dt) (initial rate, *M*/l per sec).

| *Addend* = | 0.005 | 0.01 | 0.02 | 0.05 | 0.1 | 0.2 | 0.5 | 1.0 |
|---|---|---|---|---|---|---|---|---|
| $CH_3COOH$ | - | - | 0.007 | - | 0.017 | 0.025 | 0.046 | 0.07 |
| $CH_2ClCOOH$ | 0.0177 | 0.0276 | 0.0425 | 0.077 | 0.120 | 0.196 | 0.380 | 0.66 |
| $CHCl_2COOH$ | - | 0.068 | 0.132 | 0.300 | 0.540 | 0.995 | - | - |
| $C_2H_5COOH$ | - | 0.003 | 0.0045 | 0.0075 | 0.011 | 0.016 | 0.029 | - |
| $CH_2BrCHBrCOOH$ | - | 0.046 | 0.078 | 0.150 | 0.244 | 0.450 | - | - |
| $CH_2ClCH_2COOH$ | - | 0.008 | 0.0118 | 0.020 | 0.030 | 0.047 | 0.084 | - |
| $COOHCH_2CH_2COOH$ | - | 0.0065 | 0.0098 | 0.017 | 0.0267 | 0.041 | 0.079 | - |
| $CH_2OHCOOH$ | - | 0.0097 | 0.0147 | 0.008 | 0.038 | 0.060 | 0.113 | - |
| $COOHCOOH$ | - | 0.0725 | - | 0.32 | 0.590 | 1.07 | 2.40 | - |

Data of rates in buffer solutions ($CH_3COOH + CH_3COONa$; $COOHCOOH + COOHCOOK$; $CH_2ClCOOH + CH_2ClCOONa$) see ([10])([5]).

## SOLVENTS

Ac 25 (50, 75, 90) = $H_2O + CH_3COOH$ %.

## COMMENTS

**General.** All reaction rates tabulated for hydrogen-halogen exchange on the aliphatic carbon in ketones and in nitroalkanes are first-order in the ketone (or nitroalkane), and independent of the concentration of the halogen. The rate determining step, in the case of the ketones, is, consequently, enolization of the ketone, and the rates and rate constants listed are, consequently, the rates and rate constants of the enolization of the ketone.

(.2) ([3])([4]) give initial rates, $-dB/dt = dA/dt$, at different concentrations of the catalyzing acid or base ($CH_3COO^-$). In Ac 50 as solvent, one run was observed to 2/3 completion, with the observation that the acid-catalyzed reaction is zero-order in the ketone ([4]). The data of ([3])([4]) listed in the columns $k$ are initial *rates*, in M/l per sec, calculated from the original figures of fall of thiosulfate titer, i.e. decrease of the number of ml 0.02*N* $Na_2S_2O_3$ used for 20 ml of solution. The catalytic action of $H^+$ is representable by $kA[H^+]$ ([19]), whereas, according to ([3]), the autocatalytic effect of the HBr formed in the reaction is actually stronger than first-order, which would correspond to a rate law $k''A[H^+]\ (1 + 1.5[H^+])$. (.4) The acid-catalytic constant $k$, as defined by $kA[H^+]$, at 25°C, calculated from the data of ([8])([9]), is in good accord with ([21]), and also with the same magnitude from reaction (.2); it clearly corresponds to the rate of enolization of $CH_3COCH_3$ in acid solution, and is independent of the nature of the halogen ($Br_2$, $I_2$). According to ([8]), the initial rate of the reaction is much greater then can be accounted for on the basis of the initial acidity of the initially "neutral" solution, and corresponds to an acidity of $\sim 2 \times 10^{-5}$; however, if that amount of HCl is added from the outset, the rate corresponds to an acidity of only $3.4 \times 10^{-5}$, and with $8 \times 10^{-5}$ HCl added, it corresponds to an acidity of only $8.4 \times 10^{-5}$. Addition of $4 \times 10^{-5}$ NaOH leaves the apparent initial acidity of the "neutral" solution unchanged. In the presence of small amounts of $CH_3COO^-$, the rate remains for many hours constant at $\sim 3.5 \times 10^{-10}$ M/l per sec. According to ([20])([21]), addition of sucrose, glycerol, etc.; increases the rate, but nonelectrolytes up to 30 % have no effect on the temperature coefficient. **(.8) (.9) (.10) (.11) (.12)** Reactions (.8) and (.9), and (.10) and (.11), are consecutive reactions. For each single step, the rate is represented by $k_wA + k_xA[X]$, where $k_w$ is the first-order $k$ in pure $H_2O$ (without addend). For the consecutive reaction (.8) and (.9),

## COMMENTS *(continued)*

$2(r - 1)[c - (x/4)] / c = (1 - f)(2r - 1)e^{-k_8 t} - (1 - rf)e^{-k_9 t}$, where $r = k_9/k_8$, $f$ = equilibrium fraction of enol, $c$ = initial ketone, $x$ = equivalents Br present at final $t$. The same relation holds for the consecutive reaction pair (.10) and (.11). The separate $k$ for the two steps were evaluated from the second-step and the overall reaction. The second-step $k$ is not evaluated for reaction (.12). In all cases, the rate is independent of $[Br_2]$. (.13) - (.23) (.28) (.30) (.32) - (.36) Data listed under $k$ are *rates* $-dA/dt = dB/dt$ in M/l per sec, calculated from original figures of fall of thiosulfate titer [see (.2)]. (.38) (.39) Rates of the rate determining steps, see 402.450. (.41) Rate-determining step → $CHBr{:}NO_2^- + H_2^+$. (.42) $k$ at 35°C is extrapolated.

## LITERATURE

(1) P.D.Bartlett, *ACS* 1934, **56**, 967. (2) P.D.Bartlett, C.H.Stauffer, *ACS* 1935, **57**, 2580. (2a) R.P.Bell, E.Gelles, E.Möller, *PRS*[A] 1949, **198**, 308. (3) R.P.Bell, J.K.Thomas, *CSL* **1939**, 1573. (4) T.G.Bonner, D.P.Evans, H.B.Watson, *CSL* **1939**, 1353. (5) H.M.Dawson, J.S.Carter, *CSL* **1926**, 2282. (6) H.M.Dawson, G.V.Hall, A.Key, *CSL* **1928**, 2844. (7) H.M.Dawson, C.R.Hoskins, J.E.Smith, *CSL* **1929**, 1884. (8) H.M.Dawson, F.Powis, *CSL* 1912, **101**, 1503. (9) H.M.Dawson, F.Powis, *CSL* **1913**, 2135. (10) H.M.Dawson, E.Spivey, *CSL* **1930**, 2180.

(11) D.P.Evans, *CSL* **1936**, 785. (12) D.P.Evans, J.J.Gordon, *CSL* **1938**, 1434. (13) D.P.Evans, V.G.Morgan, H.B.Watson, *CSL* **1935**, 1167. (14) L.P.Hammett, L.Zucker, *ACS* 1939, **61**, 2779. (15) L.P.Hammett, L.Zucker, *ACS* 1939, **61**, 2791. (16) R.Junell, *ZPC*[A] 1929, **141**, 71. (17) K.J.Pedersen, F.Dansk. Videnskap. Salskap. Mat-fysiske Medt., 1932, **12**, 1. (18) O.Reitz, *ZPC*[A] 1936, **176**, 363. (19) O.Reitz, *ZPC*[A] 1937, **179**, 119. (20) F.O.Rice, C.F.Fryling, W.A.Wesolowski, *ACS* 1924, **46**, 2404. (21) F.O.Rice, M.Kilpatrick, Jr., *ACS* 1923, **45**, 1401.

# EXCHANGE

## of H for halogen on aromatic C

*Liquid phase*

Reaction type: $ArH + X_2 \rightarrow ArX + HX$

Rate measured $-dB/dt = +dM/dt$

Amounts are in M/l. Rates are in M/l per sec.
*Coded solvents, Comments, Literature, at the end of the table.

*Note:* For compounds involving more than one aromatic ring, it is understood that the substitution takes place in the ring written *last*. The position of the substituent halogen atom in the product, *if given*, is designated by a position number counted from the substituent designated in the initial reactant by the number 1.

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Unsubstituted aromatic hydrocarbons** | | | | | | | | | | | | | | |
| .1 | $C_6H_6 + Cl_2$ | Ac 99 | A = 0.5; B = 0.05 | | | $kAB$ | 24 | 1.48 | -6 | | | | | (3) |
| | | | | | | | 34.2 | 3.90 | -6 | 17 | | | | |
| | | | " | HCl | 1.31 | " | 24 | 6.7 | -6 | | | | | |
| .2 | $C_6H_6 + Br_2$ | $C_6H_6$ | 0.25 - 1 | $I_2$ | $k'B^{3/2} = kB^{3/2}[I_2]^{5/2}$ | | 25 | | | | | | * | (2a) (19) |
| | | | | | 0.086 | | $k'$ | 7.5 | -6 | | | | | |
| | | | | | 0.107 | | | 1.4 | -5 | | | | | |
| | | | | | 0.143 | | | 3.1 | -5 | | | | | |
| | | | | | 0.214 | | | 1.1 | -4 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Amount of reactant | Addend (Catalyst) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $C_6H_6 + Br_2$ *(continued)* | | | | 0.086 | | $k$ | 3.5 | -3 | | | | | |
| | | | | | 0.107 | | | 5.8 | -3 | | | | | |
| | | | | | 0.143 | | | 4.0 | -3 | | | | | |
| | | | | | 0.214 | | | 5.1 | -3 | | | | | |
| .3 | $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ | $H_2O$ | | $Br^-$ | 0.01 | $k\,AB$ | 25 | 2.8 | -3 | | | | * | (21) |
| | $C_6H_6 + HBrO \rightarrow C_6H_5Br + H_2O$ | $H_2O$ | | $HClO_4$ | 0.01 | $k\,AB$ | 25 | 9.5 | -2 | | | | * | (21) |
| | | | | | 0.02 | | | 2.0 | -1 | | | | | |
| | | | | | 0.04 | | | 3.7 | -1 | | | | | |
| | | | | | 0.06 | | | 5.4 | -1 | | | | | |
| .4 | $C_{10}H_8 + Cl_2$ | Ac 99 | 0.0125 - 0.025 | | | $k\,AB$ | 15.3 | 6.9 | -2 | | | | * | (3) |
| | | | | | | | 24 | 1.1 | -1 | 7.5 | | | | |
| .5 | $C_{14}H_{10} + Br_2$ | $CCl_4$ | A = B = 0.016 - 0.064 | $I_2$ | 0.002 - 0.012 | $k\,AB^{3/2}[I_2]^{5/2}$ | | | | | | | * | (19) |
| | | | | | | | 25 | 1.03 | -7 | | | | | |
| | **Alkyl-substituted aromatic hydrocarbons** | | | | | | | | | | | | | |
| .6 | $C_6H_5CH_3 + Cl_2$ | Ac 99 | A = 0.1; B = 0.025 | | | | 24 | See Supplementary Table | | | | | | (3) |
| .7 | $C_6H_5CH_3 + Br_2$ | Ac 85 | 0.05 | | | | " | " | " | " | | | | (3) |
| .8 | $C_6H_5C_2H_5 + Cl_2$ | Ac 99 | A = 0.1; B = 0.025 | | | | " | " | " | " | | | | (3) |
| .9 | $C_6H_5C_2H_5 + Br_2$ | Ac 85 | 0.05 | | | | " | " | " | " | | | | (3) |
| .10 | $(CH_3)_2CHC_6H_5 + Cl_2$ | Ac 99 | A = 0.1; B = 0.025 | | | | " | " | " | " | | | | (3) |
| .11 | $(CH_3)_2CHC_6H_5 + Br_2$ | Ac 85 | 0.05 | | | | " | " | " | " | | | | (3) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .12 | $(CH_3)_3CC_6H_5 + Cl_2$ | Ac 99 | A = 0.1; B = 0.025 | | | | 24 | See Supplementary Table | | | | | | ([3]) |
| .13 | $(CH_3)_3CC_6H_5 + Br_2$ | Ac 85 | 0.05 | | | | " | " | | " | " | | | ([3]) |
| .14 | $1,2 - (CH_3)_2C_6H_4 + Cl_2$ | Ac 99 | A = 0.1; B = 0.025 | | | | " | " | | " | " | | | ([3]) |
| .15 | $1,4 - (CH_3)_2C_6H_4 + Cl_2$ | Ac 99.9 | A = 0.1; B = 0.025 | | | | " | " | | " | " | | | ([3]) |
| .16 | $1,2 - (CH_3)_2C_6H_4 + Br_2$ | Ac 99 | 0.2 | | | | " | " | | " | " | | | ([3]) |
| .17 | $1,3 - (CH_3)_2C_6H_4 + Br_2$ | Ac 99.9 | 0.0125 - 0.2 | | | | " | " | | " | " | | | ([3]) |
| .18 | $(CH_3)_3C_6H_3 + Br_2$ | Ac 99.9 | 0.025 | $x =$ | 5 % | $kAB^2$ | " | 1.45 | +1 | | | | * | ([20]) |
| | | | | | 15 | | | 1.56 | +1 | | | | | |
| | | | | | 30 | | | 1.45 | +1 | | | | | |
| | | | | | 50 | | | 1.37 | +1 | | | | | |
| | **Alkoxy-substituted aromatic hydrocarbons** | | | | | | | | | | | | | |
| .19 | $CH_3OC_6H_5 + Br_2$ | $CH_3COOH$ | 0.0125 | | | $kAB^2$ | 24 | See Supplementary Table | | | | | | ([20]) |
| .20 | $p$-$CH_3OC_6H_4CH_3 + Br_2$ | " | " | | | $kAB^2$ | " | " | | " | " | | | ([20]) |
| | **Amide-substituted aromatic hydrocarbons** | | | | | | | | | | | | | |
| .21 | $CH_3CONHC_6H_5 + Br_2 \rightarrow (p)$ | $CH_3COOH$ | A = B = 0.025 | $x =$ | 5 % | $kAB^2$ | 24 | 1.48 | +1 | | | | * | ([20]) |
| | | | | | 15 | | " | 1.57 | +1 | | | | | |
| | | | | | 30 | | " | 1.18 | +1 | | | | | |
| | | | | | 50 | | " | 6.2 | +0 | | | | | |
| .22 | $CH_3CONHC_6H_4CH_3 + Br_2$ | $CH_3COOH$ | 0.0125 - 0.1 | | | $kAB^2$ | " | See Supplementary Table | | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .23 | $CCl_3CONHC_6H_5 + Cl_2$ | Ac 99 | A = 0.0075; B = 0.0025 | HCl | 0.0125 | $k$AB | 20 | 9.6 | -3 | | | | | (2) |
| | | | | | | | 30 | 1.8 | -2 | | | | | |
| .24 | $CCl_3CON(CH_3)C_6H_5 + Cl_2$ | Ac 99 | A = 0.075; B = 0.005 | HCl | 0.0125 | $k$AB | 20 | 5.6 | -4 | | | | | (2) |
| .25 | $p$-$CH_3C_6H_4SO_2NHC_6H_5 + Cl_2$ | Ac 99 | A = B = 0.0025 | HCl | 0.0125 | $k$AB | 20 | 1.85 | 0 | | | | | (2) |
| .26 | $p$-$CH_3C_6H_4SO_2N(CH_3)C_6H_5 + Cl_2$ | Ac 99 | A = B = 0.0025 | HCl | 0.0125 | $k$AB | 20 | 4.35 | -2 | | | | | (2) |
| | **Disubstituted aromatic hydrocarbons** **Alkoxyl, Carboxyl** | | | | | | | | | | | | | |
| .27 | o-$CH_3OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.8 | -2 | | | | | (7) |
| .28 | m-$CH_3OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.01 - 0.02; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 2.6 | -2 | | | | | (14) |
| .29 | $p$-$CH_3OC_6H_4COOH + Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.4 | -3 | | | | | (1)(2)(7) |
| | | | | | | | 30 | 1.48 | -2 | | | | | |
| .30 | m-$C_2H_5OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.01 - 0.02; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.5 | -2 | | | | | (14) |
| .31 | $p$-$C_2H_5OC_6H_4COOH(1) + Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.46 | -2 | | | | | (1) |
| .32 | m-$C_3H_7OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.8 | -2 | | | | | (14) |
| .33 | $p$-$C_3H_7OC_6H_4COOH(1) + Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.6 | -2 | | | | | (1) |
| .34 | m-$(CH_3)_2CHOC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.01 - 0.02; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.06 | -1 | | | | | (14) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Adeend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .35 | $p$-$(CH_3)_2CHOC_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.3 | -2 | | | | | ([1]) |
| .36 | $m$-$C_4H_9OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015 - 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 6.0 | -2 | | | | | ([14]) |
| .37 | $p$-$C_4H_9OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0025; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.61 | -2 | | | | | ([1]) |
| .38 | $p$-$C_2H_5CH(CH_3)OC_6H_4COOH(1) + Cl_2 \rightarrow (2)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.56 | -2 | | | | | ([2]) |
| .39 | $m$-$C_5H_{11}OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0225 - 0.0150; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.83 | -2 | | | | | ([14]) |
| .40 | $p$-$C_5H_{11}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.61 | -2 | | | | | ([6]) |
| .41 | $m$-$C_6H_{13}OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0150; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.9 | -2 | | | | | ([14]) |
| .42 | $p$-$C_6H_{13}C_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.6 | -2 | | | | | ([6]) |
| .43 | $m$-$C_7H_{15}C_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.75 | -2 | | | | | ([14]) |
| .44 | $p$-$C_7H_{15}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.58 | -2 | | | | | ([6]) |
| .45 | $m$-$C_8H_{17}OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.8 | -2 | | | | | ([14]) |
| .46 | $p$-$C_8H_{17}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.53 | -2 | | | | | ([6]) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .47 | $m$-$C_9H_{19}OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.75 | -2 | | | | | (14) |
| .48 | $m$-$C_{12}H_{25}OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.63 | -2 | | | | | (14) |
| .49 | $p$-$C_{16}H_{33}OC_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0025; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.86 | -2 | | | | | (6) |
| .50 | $o$-$C_6H_5CH_2OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 4.5 | -2 | | | | | (7) |
| .51 | $m$-$C_6H_5CH_2OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.9 | -2 | | | | | (14) |
| .52 | $p$-$C_6H_5CH_2OC_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 5.23 | -3 | | | | (1) | (7) |
| .53 | $m$-$C_6H_5CH_2CH_2OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015 - 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.8 | -2 | | | | | (14) |
| .54 | $p$-$C_6H_5CH_2CH_2OC_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 8.8 | -3 | | | | | (6) |
| .55 | $m$-$C_6H_5CH_2CH_2CH_2OC_6H_4COOH + Cl_2$ | Ac 99 | A = 0.015 - 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 4.67 | -2 | | | | | (14) |
| .56 | $p$-$C_6H_5CH_2CH_2CH_2OC_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.27 | -2 | | | | | (6) |
| .57 | $o$-($p$-$CH_3C_6H_4CH_2O$)$C_6H_4COOH + Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 6.2 | -2 | | | | | (6) |
| .58 | $p$-($o$-$CH_3C_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.75 | -3 | | | | | (6) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .59 | $p$-($m$-$CH_3C_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.6 | -3 | | | | | (7) |
| .60 | $p$-($p$-$CH_3C_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.35 | -3 | | | | | (7) |
| .61 | $o$-($p$-$FC_6H_4CH_2O$)$C_6H_4COOH$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.65 | -2 | | | | | (7) |
| .62 | $m$-($p$-$FC_6H_4CH_2O$)$C_6H_4COOH$ + $Cl_2$ | Ac 99 | A = 0.015 - 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.56 | -2 | | | | | (14) |
| .63 | $p$-($o$-$FC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 2.67 | -3 | | | | | (7) |
| .64 | $p$-($m$-$FC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 2.62 | -3 | | | | | (7) |
| .65 | $p$-($p$-$FC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 4.37 | -3 | | | | | (6) |
| .66 | $o$-($p$-$ClC_6H_4CH_2O$)$C_6H_4COOH$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.05 | -2 | | | | | (6) |
| .67 | $m$-($p$-$ClC_6H_4CH_2O$)$C_6H_4COOH$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.20 | -2 | | | | | (14) |
| .68 | $p$-($o$-$ClC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 2.53 | -3 | | | | | (6) |
| .69 | $p$-($m$-$ClC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 2.55 | -3 | | | | | (6) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .70 | $p$-($p$-$ClC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.33 | -3 | | | | | ([6]) |
| .71 | $o$-($p$-$BrC_6H_4CH_2O$)$C_6H_4COOH$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.1 | -2 | | | | | ([6]) |
| .72 | $m$-($p$-$BrC_6H_4CH_2O$)$C_6H_4COOH$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.15 | -2 | | | | | ([14]) |
| .73 | $p$-($m$-$BrC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.65 | -3 | | | | | ([6]) |
| .74 | $p$-($p$-$BrC_6H_4CH_2O$)$C_6H_4COOH$(1) + $Cl_2 \rightarrow$ (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.38 | -3 | | | | | ([6]) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Disubstituted aromatic hydrocarbons Alkoxy, Benzoyl** | | | | | | | | | | | | | |
| .75 | $p$-$C_6H_5COC_6H_4OCH_3$(1) + $Cl_2$ → (2) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$ AB | 20 | 2.10 | -2 | | | | | (8) |
| .76 | $p$-$C_6H_5COC_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 4.00 | -2 | | | | (12) | (8) |
| | | | | | | | 30 | 7.38 | -2 | 10.9 | 6 | 6 | | |
| .77 | $p$-$C_6H_5COC_6H_4OC_4H_9$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 4.37 | -2 | | | | | (8) |
| .78 | $p$-$C_6H_5COC_6H_4OC_5H_{11}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 4.27 | -2 | | | | (12) | (8) |
| | | | | | | | 35 | 1.08 | -1 | 10.9 | 6 | 6 | | |
| .79 | $p$-$C_6H_5COC_6H_4OC_7H_{15}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 4.48 | -2 | | | | | (8) |
| .80 | $p$-$C_6H_5COOC_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.23 | -1 | | | | | (12) |
| | | | | | | | 35 | 2.88 | -1 | 10.1 | 4.7 | 6 | | |
| .81 | $p$-($m$-$CH_3C_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 2.57 | -2 | | | | | (8) |
| .82 | $p$-($p$-$CH_3C_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 2.80 | -2 | | | | | (8) |
| .83 | $p$-($p$-$CH_3OC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 7.73 | -2 | | | | | (8) |
| .84 | $p$-($p$-$CH_3OC_6H_4CO$)$C_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.16 | -1 | | | | | (8) |



942151 O—51——23

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .85 | $p$-($p$-$CH_3OC_6H_4CO$)$C_6H_4OCH_2CH_2Cl$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$ AB | 20 | 4.65 | -2 | | | | | (8) |
| .86 | $p$-($p$-$CH_3OC_6H_4CO$)$C_6H_4OC_3H_7$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.22 | -1 | | | | | (8) |
| .87 | $p$-($p$-$CH_3OC_6H_4CO$)$C_6H_4OC_4H_9$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.22 | -1 | | | | | (8) |
| .88 | $p$-($p$-$CH_3OC_6H_4CO$)$C_6H_4OC_5H_{11}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.26 | -1 | | | | | (8) |
| .89 | $p$-($p$-$C_2H_5OC_6H_4CO$)$C_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.57 | -1 | | | | | (8) |
| .90 | $p$-($p$-$C_2H_5OC_6H_4CO$)$C_6H_4OC_4H_9$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.64 | -1 | | | | | (8) |
| .91 | $p$-($p$-$C_2H_5OC_6H_4CO$)$C_6H_4OC_5H_{11}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.62 | -1 | | | | | (8) |
| .92 | $p$-($p$-$C_3H_7OC_6H_4CO$)$C_6H_4OC_3H_7$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.71 | -1 | | | | | (8) |
| .93 | $p$-($p$-$(CH_3)_2CHOC_6H_4CO$)$C_6H_4OCH(CH_3)_2$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 3.77 | -1 | | | | | (8) |
| .94 | $p$-($p$-$C_4H_9OC_6H_4CO$)$C_6H_4OC_4H_9$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.75 | -1 | | | | | (8) |
| .95 | $p$-($p$-$C_5H_{11}OC_6H_4CO$)$C_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$ AB | 20 | 1.72 | -1 | | | | | (8) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .96 | $p$-($m$-$NO_2C_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.33 | -3 | | | | | (8) |
| .97 | $p$-($p$-$NO_2C_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 6.42 | -3 | | | | | (8) |
| .98 | $p$-($m$-$NO_2C_6H_4CO$)$C_6H_4OC_4H_9$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.62 | -2 | | | | | (8) |
| .99 | $p$-($o$-$FC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 9.75 | -3 | | | | | (8) |
| .100 | $p$-($m$-$FC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.30 | -2 | | | | | (8) |
| .101 | $p$-($p$-$FC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.78 | -2 | | | | | (8) |
| .102 | $p$-($o$-$ClC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 7.83 | -3 | | | | | (8) |
| .103 | $p$-($p$-$ClC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.45 | -2 | | | | | (8) |
| .104 | $p$-($p$-$ClC_6H_4CO$)$C_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 2.67 | -2 | | | | (12) | (8) |
| | | | | | | | 35 | 6.80 | -2 | 11.0 | 4.7 | 6 | | |
| .105 | $p$-($o$-$ClC_6H_4CO$)$C_6H_4OCH_2CH_2Cl$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.92 | -3 | | | | | (8) |
| .106 | $p$-($o$-$BrC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 7.67 | -3 | | | | | (8) |
| .107 | $p$-($m$-$BrC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.29 | -2 | | | | | (8) |
| .108 | $p$-($p$-$BrC_6H_4CO$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.42 | -2 | | | | | (8) |
| | **Disubstituted aromatic hydrocarbons Carboxyl, Amide** | | | | | | | | | | | | | |
| .109 | $p$-$C_2H_5CONHC_6H_4COOH$(1) + $Cl_2$ → (3) | Ac 99 | B = 0.02 | HCl | 0.05 | $k$AB | 20 | | | | | | | (4) |
| | | | A = 0.02 | | | | | 1.20 | -2 | | | | | |
| | | | 0.1 | | | | | 1.48 | -2 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .110 | $p$-$C_6H_5SO_2NHC_6H_4COOH(1) + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.06; B = 0.002 | HCl | 0.05 | $kAB$ | 20 | 3.32 | -3 | | | | | ([4]) |
| | **Disubstituted aromatic hydrocarbons Hydroxyl, Aminoalkyl** | | | | | | | | | | | | | |
| .111 | $p$-$NH_2CH_2CH_2C_6H_4OH + 2I_2$ tyramine | $H_2O$; pH 5.23 | A = 0.003; B = 0.005 | $I^-$ | 0.0334 | $kA[I_3^-]$ | 25 | 1.2 | -4 | | | | * | ([18]) |
| | | | | | 0.0408 | | " | 7.5 | -3 | | | | | ([17]) |
| | | | | | 0.0484 | | " | 5.8 | -3 | | | | | ([15]) |
| | | | | | 0.0634 | | " | 3.3 | -3 | | | | | |
| .112 | $p$-$(COO^-)CHNH_3^+CH_2C_6H_4OH + 2I_2$ | " | " | $I^-$ | 0.0334 | " | " | 8.7 | -3 | | | | * | " |
| | | | | | 0.0408 | | " | 6.3 | -3 | | | | | |
| | | | | | 0.0484 | | " | 4.7 | -3 | | | | | |
| | | | | | 0.0634 | | " | 2.7 | -3 | | | | | |
| .113 | $p$-$(COO^-)CH(NHCOCH_2NH_3^+)CH_2C_6H_4OH + 2I_2$ | " | " | $I^-$ | 0.0334 | " | " | 1.5 | -2 | | | | * | " |
| | | | | | 0.0408 | | " | 1.05 | -2 | | | | | |
| | | | | | 0.0484 | | " | 7.5 | -3 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Disubstituted aromatic hydrocarbons Hydroxyl, Halogen** | | | | | | | | | | | | | |
| .114 | $p$-$ClC_6H_4OH + 2I_2$ | $H_2O$; pH 5.23 | A = 0.003; B = 0.005 | $I^-$ | 0.0334 | $k A [I_3^-]$ | 25 | 2.25 | -3 | | | | * | (18) |
| | | | | | 0.0408 | | " | 1.35 | -3 | | | | | (17) |
| | | | | | 0.0484 | | " | 1.0 | -3 | | | | | (15) |
| | | | | | 0.0634 | | " | 5.5 | -4 | | | | | |
| | **Disubstituted aromatic hydrocarbons Alkoxyl, Nitro** | | | | | | | | | | | | | |
| .115 | $o$-$NO_2C_6H_4OCH_3 + Br_2$ | $H_2O$; pH - 2.3 | A = 0.0025 - 0.005 B = 0.002 - 0.01 | | | | | | | | | | * | (21) |
| | | | | $Br^-$ | 0.01 | $k AB$ | 25 | 5.5 | -2 | | | | | |
| .116 | $o$-$NO_2C_6H_4OCH_3 + HBrO$ | $H_2O$; pH 2.8 | " | " | " | " | " | 1.7 | -2 | | | | * | " |
| .117 | $m$-$NO_2C_6H_4OCH_3 + Cl_2$ | Ac 99 | A = 0.10; B = 0.02 | HCl | 0.0475 | $k AB$ | 20 | 8.90 | -5 | | | | | (5) |
| .118 | $p$-$NO_2C_6H_4OCH_3$(1) + $Cl_2 \rightarrow$ (2) | " | A = 0.0225; B = 0.0075 | " | 0.0375 | $k AB$ | 20 | 4.78 | -5 | | | | | (12) |
| | | | | | | | 35 | 1.63 | -4 | 14.6 | 4.2 | 6 | | |
| .119 | $m$-$NO_2C_6H_4OC_2H_5 + Cl_2$ | " | A = 0.10; B = 0.20 | " | 0.0475 | $k AB$ | 20 | 1.77 | -4 | | | | | (14) |
| .120 | $p$-$NO_2C_6H_4OC_2H_5$(1) + $Cl_2 \rightarrow$ (2) | " | A = 0.0225; B = 0.0075 | " | 0.0375 | $k AB$ | 20 | 9.8 | -5 | | | | | (12) (2) |
| | | | | | | | 35 | 3.27 | -4 | 14.3 | 5.0 | 6 | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .121 | $p$-$NO_2C_6H_4OC_3H_7$(1) + $Cl_2$ → (2) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.10 | -4 | | | | | ([1]) |
| .122 | $p$-$NO_2C_6H_4OCH(CH_3)_2$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 2.35 | -4 | | | | | ([12]) |
| | | | | | | | 35 | 7.38 | -4 | 13.8 | 4.7 | 6 | | |
| | **Disubstituted aromatic hydrocarbons Alkoxyl, Sulfo** | | | | | | | | | | | | | |
| .123 | $p$-($p$-$CH_3OC_6H_4SO_2$)$C_6H_4OCH_3$(1) + $Cl_2$ → (2) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.83 | -3 | | | | | ([8]) |
| .124 | $p$-($p$-$C_2H_5OC_6H_4SO_2$)$C_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 3.72 | -3 | | | | | ([8]) |
| .125 | $p$-($p$-$C_3H_7OC_6H_4SO_2$)$C_6H_4OC_3H_7$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.12 | -3 | | | | | ([8]) |
| .126 | $p$-($p$-$(CH_3)_2CHOC_6H_4SO_2$)$C_6H_4OCH(CH_3)_2$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 8.93 | -3 | | | | | ([8]) |
| .127 | $p$-($p$-$C_4H_9OC_6H_4SO_2$)$C_6H_4OC_4H_9$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.12 | -3 | | | | | ([8]) |
| .128 | $p$-($p$-$C_5H_{11}OC_6H_4SO_2$)$C_6H_4OC_5H_{11}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.15 | -3 | | | | | ([8]) |
| | **Disubstituted aromatic hydrocarbons Alkoxyl, Halogen** | | | | | | | | | | | | | |
| .129 | $p$-$FC_6H_4OCH(CH_3)_2$(1) + $Cl_2$ → (2) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.58 | -1 | | | | | ([12]) |
| | | | | | | | 35 | 3.62 | -1 | 9.9 | 3.7 | 6 | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .130 | o-$ClC_6H_4OCH_3$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.40 | -2 | | | | | (7) |
| .131 | m-$ClC_6H_4OCH_3$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.20 | -2 | | | | | (5) |
| .132 | p-$ClC_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | B = 0.0075; A = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 2.2 | -2 | | | | (1) | (12) |
| | | | " | | 0.0600 | | " | 2.3 | -2 | | | | | |
| | | | " | | 0.0075 | | " | 2.0 | -2 | | | | | |
| | | | 0.0225 | HCl | 0.0375 | " | 20 | 2.0 | -2 | | | | | " |
| | | | " | | " | | 35 | 5.2 | -2 | 11.3 | 6.0 | 6 | | |
| | | Ac 98 | A = B = 0.0075 | HCl | 0.0375 | " | 20 | 3.7 | -2 | | | | | |
| .133 | o-$ClC_6H_4OC_2H_5$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | " | 0.0375 | $k$AB | 20 | 1.45 | -1 | | | | | (2) |
| .134 | p-$ClC_6H_4OC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 3.88 | -2 | | | | | (12) |
| | | | | | | | 35 | 9.47 | -2 | 10.8 | 4.5 | 6 | | |
| .135 | o-$ClC_6H_4OC_3H_7$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.68 | -1 | | | | | (6) |
| .136 | p-$ClC_6H_4OC_3H_7$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 2.05 | -1 | | | | | (2) |
| .137 | o-$ClC_6H_4OCH(CH_3)_2$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 2.69 | -1 | | | | | (6) |
| .138 | p-$ClC_6H_4OCH(CH_3)_2$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 8.6 | -2 | | | | | (12) |
| | | | | | | | 35 | 2.1 | -1 | 10.5 | 6.0 | 6 | | |
| .139 | o-$ClC_6H_4OC_4H_9$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.7 | -1 | | | | | (6) |
| .140 | m-$ClC_6H_4OC_4H_9$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 4.53 | -2 | | | | | (2) |
| .141 | p-$ClC_6H_4OCH(CH_3)(C_2H_5)$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.50 | -2 | | | | | (2) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .142 | o-$ClC_6H_4OC_5H_{11}$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 1.64 | -1 | | | | | (6) |
| .143 | p-$ClC_6H_4OC_5H_{11}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.60 | -2 | | | | | (6) |
| .144 | p-$ClC_6H_4OC_6H_{13}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.62 | -2 | | | | | (6) |
| .145 | p-$ClC_6H_4OC_7H_{15}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.57 | -2 | | | | | (6) |
| .146 | p-$ClC_6H_4OC_{16}H_{33}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.43 | -2 | | | | | (6) |
| .147 | p-$ClC_6H_4OCH_2COOH$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 8.2 | -4 | | | | | (12) |
| | | | | | | | 35 | 2.43 | -3 | 12.9 | 3.8 | 6 | | |
| .148 | p-$ClC_6H_4OCH_2COOCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 7.7 | -4 | | | | | (12) |
| | | | | | | | 35 | 2.20 | -3 | 13.0 | 5.9 | 6 | | |
| .149 | p-$ClC_6H_4OCH_2COOC_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 8.0 | -4 | | | | | (12) |
| | | | | | | | 35 | 2.35 | -3 | 12.8 | 3.2 | 6 | | |
| | **Disubstituted aromatic hydrocarbons Arylalkoxyl, Halogen** | | | | | | | | | | | | | |
| .150 | o-$C_6H_5CH_2OC_6H_4F$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 6.02 | -2 | | | | | (9) |
| .151 | p-$C_6H_5CH_2OC_6H_4F$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 2.47 | -2 | | | | | (12) |
| | | | | | | | 35 | 6.22 | -2 | 11.0 | 4.3 | 6 | | |
| .152 | o-(p-$CH_3C_6H_4CH_2O$)$C_6H_4F$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 8.18 | -2 | | | | | (9) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .153 | $p$-($p$-$CH_3C_6H_4CH_2O$)$C_6H_4F$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 3.72 | -2 | | | | | (9) |
| .154 | $o$-($p$-$NO_2C_6H_4CH_2O$)$C_6H_4F$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.28 | -2 | | | | | (9) |
| .155 | $p$-($p$-$NO_2C_6H_4CH_2O$)$C_6H_4F$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 3.63 | -2 | | | | | (9) |
| .156 | $p$-($p$-$NO_2C_6H_4CH_2O$)$C_6H_4F$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 5.0 | -3 | | | | | (12) |
| | | | | | | | 35 | 1.35 | -2 | 11.9 | 4.2 | 6 | | |
| .157 | $p$-($p$-$ClC_6H_4CH_2O$)$C_6H_4F$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.42 | -2 | | | | | (12) |
| | | | | | | | 35 | 3.72 | -2 | 11.4 | 5.0 | 6 | | |
| .158 | $o$-($p$-$BrC_6H_4CH_2O$)$C_6H_4F$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 3.48 | -2 | | | | | (9) |
| .159 | $p$-($p$-$BrC_6H_4CH_2O$)$C_6H_4F$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.52 | -2 | | | | | (9) |
| .160 | $m$-$C_6H_5CH_2OC_6H_4Cl$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 8.8 | -1 | | | | | (14) |
| .161 | $p$-$C_6H_5CH_2OC_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.31 | -2 | | | | | (12) |
| | | | | | | | 35 | 3.40 | -2 | 11.4 | 4.3 | 6 | | |
| .162 | $o$-($m$-$CH_3C_6H_4CH_2O$)$C_6H_4Cl$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 7.25 | -2 | | | | | (9) |
| .163 | $o$-($p$-$CH_3C_6H_4CH_2O$)$C_6H_4Cl$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 7.17 | -2 | | | | | (9) |
| .164 | $p$-($p$-$CH_3C_6H_4CH_2O$)$C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.94 | -2 | | | | (9) | (7) |
| .165 | $o$-($p$-$C_2H_5C_6H_4CH_2O$)$C_6H_4Cl$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 7.05 | -2 | | | | | (9) |
| .166 | $p$-($p$-$C_2H_5C_6H_4CH_2O$)$C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.93 | -2 | | | | | (9) |
| .167 | $p$-($p$-$(CH_3)_2CHC_6H_4CH_2O$)$C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.98 | -2 | | | | | (9) |

| No | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .168 | o-(p-$(CH_3)_3CC_6H_4CH_2O)C_6H_4Cl + Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 7.02 | -2 | | | | | (9) |
| .169 | p-(p-$(CH_3)_3CC_6H_4CH_2O)C_6H_4Cl$(1) → (3) | " | " | " | " | $k$AB | 20 | 1.92 | -2 | | | | | (9) |
| .170 | o-(o-$NO_2C_6H_4CH_2O)C_6H_4Cl + Cl_2$ | " | " | " | " | $k$AB | 20 | 1.05 | -2 | | | | | (6) |
| .171 | o-(p-$NO_2C_6H_4CH_2O)C_6H_4Cl + Cl_2$ | " | " | " | " | $k$AB | 20 | 1.07 | -2 | | | | (6) | (2) |
| .172 | p-(m-$NO_2C_6H_4CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 3.00 | -3 | | | | (12) | (7) |
| | | | | | | | 35 | 8.43 | -3 | 12.3 | 4.7 | 6 | | |
| .173 | p-(p-$NO_2C_6H_4CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 2.62 | -3 | | | | | (12) |
| | | | | | | | 35 | 7.43 | -3 | 12.4 | 4.7 | 6 | | |
| .174 | o-(m-$FC_6H_4CH_2O)C_6H_4Cl + Cl_2$ | " | " | " | " | $k$AB | 20 | 4.13 | -2 | | | | | (7) |
| .175 | p-(m-$FC_6H_4CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 6.57 | -3 | | | | | (7) |
| .176 | p-(p-$FC_6H_4CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.12 | -2 | | | | | (7) |
| .177 | o-(p-$ClC_6H_4CH_2O)C_6H_4Cl + Cl_2$ | " | " | " | " | $k$AB | 20 | 3.10 | -2 | | | | | (7) |
| .178 | p-(o-$ClC_6H_3CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 5.77 | -3 | | | | | (7) |
| .179 | p-(m-$ClC_6H_4CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 6.20 | -3 | | | | | (7) |
| .180 | p-(p-$ClC_6H_4CH_2O)C_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 7.8 | -3 | | | | | (12) |
| | | | | | | | 35 | 2.10 | -2 | 11.9 | 6.0 | 6 | | |
| .181 | o-(p-$BrC_6H_4CH_2O)C_6H_4Cl + Cl_2$ | " | " | " | " | $k$AB | 20 | 3.08 | -2 | | | | | (7) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .182 | $p$-($m$-$BrC_6H_4CH_2O$)$C_6H_4Cl$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 6.28 | -3 | | | | | (7) |
| .183 | $p$-(1,2 - $Cl_2$ - $C_6H_3$ - 4 - $CH_2O$)$C_6H_4Cl$(1) + $Cl_2$ → (3) | | " | " | " | $k$AB | 20 | 3.25 | -2 | | | | | (9) |
| .184 | $p$-(1,3 - $Cl_2$ - $C_6H_3$ - 4 - $CH_2O$)$C_6H_4Cl$(1) + $Cl_2$ → (3) | | " | " | " | $k$AB | 20 | 8.05 | -2 | | | | | (9) |
| .185 | $o$-$BrC_6H_4OCH_3$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 9.10 | -2 | | | | | (7) |
| .186 | $p$-$BrC_6H_4OCH_3$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 2.09 | -2 | | | | | (7) |
| .187 | $p$-$BrC_6H_4OCH_2CH_2Br$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.43 | -3 | | | | | (7) |
| .188 | $p$-$BrC_6H_4OCH_2CH_2CH_2Br$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 1.37 | -2 | | | | | (7) |
| .189 | $p$-$BrC_6H_4OCH(CH_3)C_2H_5$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.57 | -2 | | | | | (6) |
| .190 | $p$-$BrC_6H_4OC_{16}H_{33}$(1) + $Cl_2$ → (2) | " | " | " | " | $k$AB | 20 | 4.45 | -2 | | | | | (6) |
| .191 | $p$-$C_6H_5CH_2OC_6H_4Br$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.42 | -2 | | | | | (7) |
| .192 | $p$-($p$-$CH_3C_6H_4CH_2O$)$C_6H_4Br$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 1.95 | -2 | | | | | (7) |
| .193 | $o$-($o$-$NO_2C_6H_4CH_2O$)$C_6H_4Br$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.26 | -2 | | | | | (7) |
| .194 | $o$-($m$-$NO_2C_6H_4CH_2O$)$C_6H_4Br$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.47 | -2 | | | | | (7) |
| .195 | $o$-($p$-$NO_2C_6H_4CH_2O$)$C_6H_4Br$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 1.25 | -2 | | | | | (7) |
| .196 | $p$-($m$-$NO_2C_6H_4CH_2O$)$C_6H_4Br$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 3.35 | -3 | | | | | (7) |
| .197 | $p$-($p$-$NO_2C_6H_4CH_2O$)$C_6H_4Br$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 2.95 | -3 | | | | | (7) |
| .198 | $o$-($p$-$ClC_6H_4CH_2O$)$C_6H_4Br$ + $Cl_2$ | " | " | " | " | $k$AB | 20 | 3.60 | -2 | | | | | (7) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .199 | $p$-($p$-$ClC_6H_4CH_2O$)$C_6H_4Br$(1) + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$AB | 20 | 8.68 | -3 | | | | | (7) |
| | **Disubstituted aromatic hydrocarbons Amide, Halogen** | | | | | | | | | | | | | |
| .200 | $p$-$CH_3CONHC_6H_4F$(1) + $Cl_2$ → (3) | Ac 99 | B = 0.02; A = 0.02<br>0.04<br>0.06 | HCl | 0.0475 | $k$AB | 20 | 6.03<br>6.43<br>6.83 | -3<br>-3<br>-3 | | | | | (9) |
| .201 | $p$-$C_6H_5CONHC_6H_4F$(1) + $Cl_2$ → (3) | " | A = B = 0.02 | " | " | $k$AB | 20 | 5.40 | -3 | | | | | (9) |
| .202 | $p$-$C_6H_5SO_2NHC_6H_4F$(1) + $Cl_2$ → (3) | " | B = 0.02; A = 0.02<br>0.04<br>0.06 | " | " | $k$AB | 20 | 3.07<br>3.10<br>3.52 | -3<br>-3<br>-3 | | | | | (9) |
| .203 | $p$-$CH_3CONHC_6H_4Cl$(1) + $Cl_2$ → (3) | " | B = 0.02; A = 0.02<br>0.04<br>0.06 | " | 0.05 | $k$AB | 20 | 6.08<br>6.85<br>7.75 | -3<br>-3<br>-3 | | | | | (4) |
| .204 | $p$-$C_2H_5CONHC_6H_4Cl$(1) + $Cl_2$ → (3) | " | A = 0.10; B = 0.02 | " | " | $k$AB | 20 | 1.58 | -2 | | | | | (4) |
| .205 | $p$-$C_6H_5CONHC_6H_4Cl$(1) + $Cl_2$ → (3) | " | " | " | " | $k$AB | 20 | 6.08 | -3 | | | | | (4) |
| .206 | $p$-$C_6H_5SO_2NHC_6H_4Cl$(1) + $Cl_2$ → (3) | " | B = 0.02; A = 0.02 - 0.06 | | " | $k$AB | 20 | 3.41 | -3 | | | | | (4) |
| .207 | $p$-$CH_3C_6H_4SO_2NHC_6H_4Cl$(1) + $Cl_2$ → (3) | " | B = 0.02; A = 0.02,<br>0.10 | " | " | $k$AB | 20 | 4.73<br>5.18 | -3<br>-3 | | | | | (4) |
| .208 | $p$-$CCl_3CONHC_6H_4Cl$(1) + $Cl_2$ → (3) | " | A = B = 0.02 | " | " | $k$AB | 20 | 1.95 | -5 | | | | | (4) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .209 | $p$-$CH_3CONHC_6H_4Br(1) + Cl_2 \rightarrow (3)$ | Ac 99 | B = 0.02; A = 0.02<br>0.10 | HCl | 0.05 | $k$AB | 20 | 6.97<br>8.80 | -3<br>-3 | | | | | (4) |
| .210 | $p$-$C_2H_5CONHC_6H_4Br(1) + Cl_2 \rightarrow (3)$ | " | A = 0.10; B = 0.02 | " | " | $k$AB | 20 | 1.74 | -2 | | | | | (4) |
| .211 | $p$-$C_6H_5SO_2NHC_6H_4Br(1) + Cl_2 \rightarrow (3)$ | " | A = 0.06; B = 0.02; | " | " | $k$AB | 20 | 3.78 | -3 | | | | | (4) |
| | **Three substituents Alkyl, Alkoxy, Nitro** | | | | | | | | | | | | | |
| .212 | $1 - CH_3 - 2 - CH_3O - 3 - NO_2 - C_6H_3 + Cl_2$ | Ac 99 | A = 0.10; B = 0.02 | HCl | 0.0475 | $k$AB | 20 | 2.05 | -4 | | | | | (14) |
| .213 | $1 - CH_3 - 4 - CH_3O - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$ | " | A = 0.12; B = 0.04 | " | 0.05 | $k$AB | 20 | 3.67 | -4 | | | | | (10) |
| .214 | $1 - CH_3 - 2 - C_2H_5O - 3 - NO_2 - C_6H_3 + Cl_2$ | " | A = 0.10; B = 0.02 | " | 0.0475 | $k$AB | 20 | 4.67 | -4 | | | | | (14) |
| .215 | $1 - CH_3 - 4 - C_2H_5O - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$ | " | A = 0.12; B = 0.04 | " | 0.05 | $k$AB | 20 | 7.00 | -4 | | | | | (10) |
| .216 | $1 - CH_3 - 4 - (CH_3)_2CHO - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$AB | 20 | 1.25 | -3 | | | | | (10) |
| .217 | $1 - CH_3 - 4 - C_4H_9O - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$AB | 20 | 7.67 | -4 | | | | | (10) |
| | **Three substituents Alkyl, Alkoxy, Halogen** | | | | | | | | | | | | | |
| .218 | $1 - CH_3 - 2 - CH_3O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | Ac 99 | B = 0.0075; A = 0.0225<br>"<br>" | HCl | 0.0375<br>0.01<br>" | $k$AB | 20<br>"<br>35 | 7.27<br>6.83<br>1.64 | -2<br>-2<br>-1 | 10.5 | 4.8 | 6 | | (10) (11) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .218 | *(continued)* | | 0.0075 | | 0.0375 | | 20 | 7.67 | -2 | | | | | |
| .219 | $1 - CH_3 - 4 - CH_3O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | " | $k$ AB | 20 | 1.19 | -1 | | | | | (10) |
| .220 | $1 - CH_3 - 2 - C_2H_5O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$ AB | 20 | 1.44 | -1 | | | | | (10) |
| .221 | $1 - CH_3 - 4 - C_2H_5O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$ AB | 20 | 2.2 | -1 | | | | | (10) |
| .222 | $1 - CH_3 - 2 - C_3H_7O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$ AB | 20 | 1.52 | -1 | | | | | (10) |
| .223 | $1 - CH_3 - 2 - (CH_3)_2CHO - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$ AB | 20 | 2.36 | -1 | | | | | (10) |
| .224 | $1 - CH_3 - 2 - C_5H_{11}O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$ AB | 20 | 1.54 | -1 | | | | | (10) |
| .225 | $1 - CH_3 - 2 - C_6H_5CH_2O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | " | " | " | $k$ AB | 20<br>35 | 3.63<br>8.92 | -2<br>-2 | 10.7 | 3.8 | 6 | | (11) |
| .226 | $1 - CH_3 - 2 - (p\text{-}CH_3C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | B = 0.0075; A = 0.0075<br>0.0225 | " | " | $k$ AB | 20 | 5.78<br>5.30 | -2<br>-2 | | | | | (10) |
| .227 | $1 - CH_3 - 4 - (p\text{-}CH_3C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$ | " | B = 0.0075; A = 0.0225<br>0.0375 | " | " | $k$ AB | 20 | 9.12<br>8.63 | -2<br>-2 | | | | | (10) |

| No | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .228 | 1 - $CH_3$ - 2 - (*p*-$C_2H_5C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | *k* AB | 20 | 5.30 | -2 | | | | | (10) |
| .229 | 1 - $CH_3$ - 4 - (*p*-$C_2H_5C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | B = 0.0075; A = 0.0225<br>0.0375 | " | " | *k* AB | 20 | 9.08<br>8.75 | -2<br>-2 | | | | | (10) |
| .230 | 1 - $CH_3$ - 2 - (*p*-$(CH_3)_3CC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | A = 0.0225; B = 0.0075 | " | " | *k* AB | 20 | 5.13 | -2 | | | | | (10) |
| .231 | 1 - $CH_3$ - 2 - (*o*-$NO_2C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | *k* AB | 20 | 6.38 | -3 | | | | | (10) |
| .232 | 1 - $CH_3$ - 2 - (*p*-$NO_2C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | A = B = 0.0075 | " | " | *k* AB | 20 | 8.80 | -3 | | | | | (10) |
| .233 | 1 - $CH_3$ - 4 - (*o*-$NO_2C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | A = 0.0225; B = 0.0075 | " | " | *k* AB | 20 | 1.27 | -2 | | | | | (10) |
| .234 | 1 - $CH_3$ - 4 - (*m*-$NO_2C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | *k* AB | 20 | 1.56 | -2 | | | | | (10) |
| .235 | 1 - $CH_3$ - 4 - (*p*-$NO_2C_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | *k* AB | 20 | 1.35 | -2 | | | | | (10) |
| .236 | 1 - $(CH_3)_3C$ - 4 - (*p*-$NO_2C_6H_4CH_2O$) - 5 - Cl - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | *k* AB | 20<br>35 | 4.85<br>1.35 | -3<br>-2 | 12.2 | 7.2 | 6 | | (13) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .237 | 1 - $CH_3$ - 2 - (m-$FC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$ AB | 20 | 1.82 | -2 | | | | | (10) |
| .238 | 1 - $CH_3$ - 4 - (m-$FC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 3.17 | -2 | | | | | (10) |
| .239 | 1 - $CH_3$ - 2 - (o-$ClC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 1.53 | -2 | | | | | (10) |
| .240 | 1 - $CH_3$ - 2 - (m-$ClC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 1.72 | -2 | | | | | (10) |
| .241 | 1 - $CH_3$ - 2 - (p-$ClC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 2.30 | -2 | | | | | (10) |
| .242 | 1 - $CH_3$ - 4 - (o-$ClC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 2.60 | -2 | | | | | (10) |
| .243 | 1 - $CH_3$ - 4 - (p-$ClC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 3.72 | -2 | | | | | (10) |
| .244 | 1 - $CH_3$ - 2 - (p-$BrC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 2.23 | -2 | | | | | (10) |
| .245 | 1 - $CH_3$ - 4 - (p-$BrC_6H_4CH_2O$) - 5 - Br - $C_6H_3$ + $Cl_2$ → (3) | " | " | " | " | $k$ AB | 20 | 3.67 | -2 | | | | | (10) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Three substituents Alkoxy, Halogen, Halogen** | | | | | | | | | | | | | |
| .246 | 1 - $CH_3O$ - 2,4 - $Cl_2$ - $C_6H_3$ + $Cl_2$ → (6) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | $k$ AB | 20 | 5.2 | -5 | | | | | (13) |
| | | | | | | | 35 | 1.72 | -4 | 14.3 | 2.7 | 6 | | |
| .247 | 1 - $CH_3O$ - 3,5 - $Cl_2$ - $C_6H_3$ + $Cl_2$ | " | B = 0.0075; A = 0.0075 | " | " | $k$ AB | 20 | 1.41 | -1 | | | | | (14) |
| | | | 0.0225 | | | | | 1.19 | -1 | | | | | |
| .248 | 1 - $C_2H_5O$ - 2,4 - $Cl_2$ - $C_6H_3$ + $Cl_2$ → (6) | " | A = 0.0225; B = 0.0075 | " | " | $k$ AB | 20 | 1.06 | -4 | | | | | (13) |
| | | | | | | | 35 | 3.43 | -4 | 14.0 | 3.3 | 6 | | |
| .249 | 1 - $C_3H_7O$ - 2,4 - $Cl_2$ - $C_6H_3$ + $Cl_2$ → (6) | " | " | " | " | $k$ AB | 20 | 1.12 | -4 | | | | | (13) |
| | | | | | | | 35 | 3.60 | -4 | 14.1 | 4.2 | 6 | | |
| .250 | 1 - $(CH_3)_2CHO$ - 2,4 - $Cl_2$ - $C_6H_3$ + $Cl_2$ → (6) | " | " | " | " | $k$ AB | 20 | 1.58 | -4 | | | | | (13) |
| | | | | | | | 35 | 4.93 | -4 | 13.6 | 2.2 | 6 | | |
| .251 | 1 - $C_6H_5CH_2O$ - 2,4 - $Cl_2$ - $C_6H_3$ + $Cl_2$ → (6) | " | A = 0.12; B = 0.04 | " | 0.0475 | $k$ AB | 20 | 1.67 | -5 | | | | | (10) |
| .252 | 1 - $C_6H_5CH_2O$ - 2,5 - $Cl_2$ - $C_6H_3$ + $Cl_2$ | " | A = 0.0225; B = 0.0075 | " | 0.0375 | $k$ AB | 20 | 5.33 | -3 | | | | | (14) |
| .253 | 1 - (*p*-$CH_3C_6H_4CH_2O$) - 2,5 - $Cl_2$ - $C_6H_3$ + $Cl_2$ | " | A = 0.015; B = 0.0075 | " | " | $k$ AB | 20 | 7.63 | -3 | | | | | (14) |
| .254 | 1 - (*m*-$FC_6H_4CH_2O$) - 2,5 - $Cl_2$ - $C_6H_3$ + $Cl_2$ | " | " | " | " | $k$ AB | 20 | 2.87 | -3 | | | | | (14) |
| .255 | 1 - (*p*-$FC_6H_4CH_2O$) - 2,5 - $Cl_2$ - $C_6H_3$ + $Cl_2$ | " | " | " | " | $k$ AB | 20 | 4.27 | -3 | | | | | (14) |
| .256 | 1 - (*m*-$ClC_6H_4CH_2O$) - 2,4 - $Cl_2$ - $C_6H_3$ + $Cl_2$ → (6) | " | A = 0.12; B = 0.04 | " | 0.0475 | $k$ AB | 20 | 1.67 | -5 | | | | | (10) |



942151 O—51——24

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .257 | 1 - (*p*-$BrC_6H_4CH_2O$) - 3,5 - $Cl_2$ - $C_6H_4$ + $Cl_2$ | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | *k* AB | 20 | 6.17 | -2 | | | | | (14) |
| | **Four substituents** | | | | | | | | | | | | | |
| .258 | 1 - $COOHCH_2O$ - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H_2$ + $Cl_2$ → (2) | Ac 99 | A = 0.0225; B = 0.0075 | HCl | 0.0375 | *k* AB | 20<br>35 | 1.39<br>3.65 | -2<br>-2 | 11.5 | 5.3 | 6 | | (13) |
| | **Five substituents** | | | | | | | | | | | | | |
| .259 | 1 - $CH_3O$ - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - $NO_2$ - $C_6H$ + $Cl_2$ | Ac 99 | A = 0.04; B = 0.02 | HCl | 0.0475 | *k* AB | 20 | 6.43 | -4 | | | | | (10) |
| .260 | 1 - $C_2H_5O$ - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - $NO_2$ - $C_6H$ + $Cl_2$ | | " | " | " | *k* AB | 20 | 1.15 | -3 | | | | | (10) |
| .261 | 1 - $C_3H_7O$ - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - $NO_2$ - $C_6H$ + $Cl_2$ | | " | " | " | *k* AB | 20 | 1.25 | -3 | | | | | (10) |
| .262 | 1 - $C_6H_5CH_2O$ - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - $NO_2$ - $C_6H$ + $Cl_2$ | | " | " | " | *k* AB | 20 | 1.21 | -3 | | | | | (10) |
| .263 | 1 - $CH_3O$ - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | | " | " | " | *k* AB | 20<br>35 | 2.08<br>4.85 | -1<br>-1 | 9.9 | 5.2 | 6 | | (13) |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .264 | 1 - $C_2H_5O$ - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | Ac 99 | A = B = 0.0075 | HCl | 0.0375 | $k$ AB | 20 | 4.50 | -1 | | | | | (10) |
| .265 | 1 - $C_3H_7O$ - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | " | A = B = 0.0075 | " | " | $k$ AB | 20 | 4.72 | -1 | | | | | (10) |
| .266 | 1 - $C_6H_5CH_2O$ - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | " | A = 0.0225; B = 0.0075 | " | " | $k$ AB | 20<br>35 | 1.19<br>2.78 | -1<br>-1 | 10.1 | 4.5 | 6 | | (13) |
| .267 | 1 - (*m*-$FC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | | " | " | " | $k$ AB | 20 | 6.42 | -2 | | | | | (10) |
| .268 | 1 - (*o*-$ClC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | | " | " | " | $k$ AB | 20 | 2.35 | -1 | | | | | (10) |
| .269 | 1 - (*m*-$ClC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | | " | " | " | $k$ AB | 20<br>35 | 5.63<br>1.41 | -2<br>-1 | 10.8 | 6.5 | 6 | | (13) |
| .270 | 1 - (*p*-$ClC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | | " | " | " | $k$ AB | 20<br>35 | 7.28<br>1.72 | -2<br>-1 | 10.4 | 4.2 | 6 | | (13) |
| .271 | 1 - (*p*-$BrC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - $Cl_2$ - $C_6H$ + $Cl_2$ | | " | " | " | $k$ AB | 20 | 7.85 | -2 | | | | | (10) |

## SUPPLEMENTARY TABLES

**(.6) - (.17)** Time (sec) for the absorption of $x$ % of the total initial halogen.

| Reaction | $x$ | sec |
|---|---|---|
| (.6) | 10 | 1975 |
| | 15 | 3240 |
| (.7) | 10 | 39800 |
| | 15 | 67600 |
| (.8) | 10 | 2390 |
| | 15 | 3830 |
| (.9) | 10 | 51500 |
| | 15 | 88000 |
| (.10) | 10 | 3820 |
| | 15 | 6360 |
| (.11) | 10 | 92500 |
| | 15 | 154000 |

| Reaction | $x$ | sec |
|---|---|---|
| (.12) | 10 | 6360 |
| | 15 | 10100 |
| (.13) | 10 | 172000 |
| | 15 | 298000 |
| (.14) | 20 | 366 |
| (.15) | 20 | 780 |
| (.16) | 20 | 16950 |
| (.17) | 20 | 181 (0.2) |
| | 20 | 48300 (0.025) |

**(.19)** *Relative* initial rates, $R$

Order of the reaction, $n$

| % $CHCl_3$ | 0 | 50 | 75 | 90 |
|---|---|---|---|---|
| $R$ | *1.00* | 0.30 | 0.12 | 0.08 |
| $n$ | 3.0 | 2.8 | 3.1 | 3.6 |

Time required for absorption of 10 % of the initial $Br_2$,

in 0.0125 M/l, 32.4 sec
0.00625 " 125 "

**(.20)** The order of the reaction varies from 2.9 to 3.2 with 5 - 20 % reaction. Time required for absorption of 10 % of the initial $Br_2$,

in 0.025 M/l, 126 sec
0.0125 " 534 "
0.00625 " 2240 "

## SUPPLEMENTARY TABLES *(continued)*

(.22) Order of the reaction, $n$

| | | | |
|---|---|---|---|
| 5 - 20 % reaction, | 0.1 - 0.05 | M/l, | $n$ = 3.3 |
| | 0.05 - 0.0125 | | 3.1 |

## SOLVENTS

Ac 99 $CH_3COOH$ 99 % + $H_2O$

## COMMENTS

**Classification.**

| | | | |
|---|---|---|---|
| *(.1) - (.5)* | *Unsubstituted aromatic hydrocarbons* | (.115) - (.122) | Alkoxy-nitro |
| *(.6) - (.26)* | *Monosubstituted aromatic hydrocarbons:* | (.123) - (.128) | Alkoxy-sulfo |
| (.6) - (.18) | Alkyl-substituted | (.129) - (.149) | Alkoxy-halogen |
| (.19) - (.20) | Alkoxy-substituted | (.150) - (.199) | Arylalkoxy-halogen |
| (.21) - (.26) | Amide-substituted | (.200) - (.211) | Amide-halogen |
| *(.27) - (.211)* | *Disubstituted aromatic hydrocarbons:* | *(.212) - (.257)* | *Trisubstituted aromatic hydrocarbons:* |
| (.27) - (.74) | Alkoxy-carboxyl | (.212) - (.217) | Alkyl-Alkoxy-Nitro |
| (.75) - (.108) | Alkoxy-benzoyl | (.218) - (.245) | Alkyl-Alkoxy-halogen |
| (.109) - (.110) | Carboxyl-amide | (.246) - (.257) | Alkoxy-halogen-halogen |
| (.111) - (.113) | Hydroxyl-aminoalkyl | *(.258)* | *Tetrasubstituted aromatic hydrocarbons* |
| (.114) | Hydroxyl-halogen | *(.259) - (.271)* | *Pentasubstituted aromatic hydrocarbons* |

## COMMENTS *(continued)*

**Reactions.** **(.2)** Selected points. The data of ([2a]) who represented them as second-order in $Br_2$ at constant $I_2$ were recalculated by ([19]) in terms of a rate constant 3/2 order in $Br_2$ and 5/2 order in $I_2$. The constancy of $k$ with varying amounts of $I_2$ is only approximate. **(.3)** The rate constant can have no absolute significance, as the reaction is actually heterogeneous, and its rate depends on the total $C_6H_6/H_2O$ interface produced by shaking. $Br^+$ is considered to be the brominating agent. **(.4)** Solvent erroneously described in original ([3]) as "1 % aqueous acetic acid"; must be $CH_3COOH$ 99 % + $H_2O$ 1 %. **(.5)** $k$ does not become constant in any experiment until the equilibrium of the addition reaction $C_{14}H_{10} + Br_2 \rightarrow C_{14}H_{10}Br_2$ has been established. Units of time and temperature not clearly stated in original, are inferred from the context. **(.18)** $k$ has maximum at ~ 15 % conversion. **(.21)** The actual total order of the reaction (at 20 % conversion) falls with increasing dilution, from 2.9 at 0.05 M/l to 2.3 at 0.00078 M/l in $CH_3COOH$. At constant dilution, 0.00625 M/l. dilution of the $CH_3COOH$ solvent with $CCl_4$ causes the rate to fall to one third between 10 % and 60 % conversion; however, on dilution with 90 % $CCl_4$, the rate in this range increases by a factor of ~ 6. The decrease of the third-order $k$ in $CH_3COOH$ is ascribed to negative catalysis by HBr.

**(.111) - (.114)** Maintained equilibria are

$I_3^- \rightleftarrows I_2 + I^-$ ($K_1$); $I_2 + H_2O \rightleftarrows HIO + H^+ + I^-$ ($K_2$);

$ROH (= A) \rightleftarrows RO^- + H^+$ ($K_3$). The rate can be represented, alternatively, by

$$k[ROH][I_3^-] = k'[ROH][HIO] + k''[RO^-][HIO],$$

with the following values of $k'$, $k''$, (converted from min to sec), and $K_3$ (at 25°C);

| Reaction | $10^7 k'$ | $10^{11} k''$ | $10^{11} K_3$ |
|---|---|---|---|
| (.111) | 1.67 | 9.68 | 1.26 |
| (.112) | 1.40 | 1.83 | 8.5 |
| (.113) | 2.00 | 6.67 | 4.0 |
| (.114) | 0.28 | 0.033 | 66 |

In terms of the equilibrium constants,

$$k = (K_1/[I^-]^2[H^+])(k'K_2 + k''K_2K_3/[H^+])$$

**(.115) (.116)** For the reaction A + HBrO, in chloroacetic acid buffers, pH 2.8, $k$ increases with the increase of total buffer concentration, from $k = 1.7 \times 10^{-2}$ to $5.0 \times 10^{-1}$.

## LITERATURE

(1) A.E.Bradfield, B.Jones, *CSL* **1928**, 1006. (2) A.E.Bradfield, B.Jones, *CSL* **1928**, 3073. (2a) L.Bruner, *ZPC* 1902, **41**, 514. (3) P.B.D. de la Mare, P.W.Robertson, *CSL* **1943**, 279. (4) B.Jones, *CSL* **1934**, 210. (5) B.Jones, *CSL* **1934**, 430. (6) B.Jones, *CSL* **1935**, 1831. (7) B.Jones, *CSL* **1935**, 1835. (8) B.Jones, *CSL* **1936**, 1854. (9) B.Jones, *CSL* **1938**, 1414. (10) B.Jones, *CSL* **1941**, 267. (11) B.Jones, *CSL* **1942**, 667. (12) B.Jones, *CSL* **1942**, 418. (13) B.Jones, *CSL* **1942**, 677. (14) B.Jones, *CSL* **1943**, 430. (15) C.H.Li, *ACS* 1942, **64**, 1147. (16) C.H.Li, *ACS* 1942, **64**, 1158. (17) C.H.Li, *ACS* 1944, **66**, 228. (18) C.H.Li, *ACS* 1948, **70**, 1716. (19) C.C.Price, *ACS* 1936, **58**, 2101; C.C.Price, C.E.Arntzen, *ACS* 1938, **60**, 2835. (20) P.W.Robertson, P.B.D. de la Mare, W.J.G.Johnston, *CSL* **1943**, 276.

(21) W.J.Wilson, F.G.Soper, *CSL* **1949**, 3376.

# EXCHANGE

## $NO_3^-$ for halogen

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $RNO_3 + X^- \rightarrow RX + NO_3^-$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CH_2NO_3 + Br^-$ | $(CH_3)_2CO$ | A = 0.025<br>B = 0.0125 | $k$ AB | 20<br>40 | 3.3<br>2.50 | −4<br>−3 | 18.4 | 1.7 | 10 |
| .2 | $p$-$CH_3C_6H_4CH_2NO_3 + Br^-$ | $(CH_3)_2CO$ | A = 0.025<br>B = 0.0125 | $k$ AB | 20<br>40 | 7.3<br>4.63 | −4<br>−3 | 18.9 | 7.2 | 10 |
| .3 | $p$-$C_2H_5C_6H_4NO_3 + Br^-$ | $(CH_3)_2CO$ | A = 0.025<br>B = 0.0125 | $k$ AB | 40 | 4.17 | −3 | | | |
| .4 | $p$-$(CH_3)_3CC_6H_4NO_3 + Br^-$ | $(CH_3)_2CO$ | A = 0.025<br>B = 0.0125 | $k$ AB | 40 | 3.66 | −3 | | | |
| .5 | $p$-$NO_2C_6H_4NO_3 + Br^-$ | $(CH_3)_2CO$ | A = 0.025<br>B = 0.0125 | $k$ AB | 20<br>40 | 9.9<br>9.1 | −4<br>−3 | 18.9 | 1.2 | 11 |
| .6 | 2, 4-$(NO_2)_2C_6H_3NO_3 + Br^-$ | $(CH_3)_2CO$ | A = 0.025<br>B = 0.0125 | $k$ AB | 20<br>40 | (7.7)<br>(6.1) | −3<br>−2 | | | |

### COMMENTS

(.3) (.4) (.5) $k$ calculated from reverse reaction and equilibrium; (.5) values of $k$ uncertain. Reverse exchange, see 332.751.

### LITERATURE

J. W. Baker, W. S. Nathan, *CSL* 1936, 236.

# EXCHANGE
## Halogen for $NO_3^-$

*Liquid phase*

Reaction type $RX + NO_3^- \rightarrow RNO_3 + X^-$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3I + AgNO_3$ | $H_2O$ | A = B = 0.025 | | $k$ AB | 24.5 | 2.66 | -6 | * | (2) |
| | | $H_2O + C_2H_5OH$ 10 vol % | | | " | " | 3.84 | -6 | | " |
| | | 20 | | | | " | 4.50 | -6 | | |
| | | 40 | | | | " | 6.34 | -6 | | |
| | | 70 | | | | " | 1.67 | -5 | | |
| | | 90 | | | | " | 1.54 | -5 | | |
| | | $C_2H_5OH$ | " | | " | " | 1.64 | -5 | | " |
| | | $CH_3OH$ | " | | " | " | 3.0 | -5 | | " |
| .2 | $CHI_3 + 3AgNO_3$ | $C_2H_5OH$ | A = 0.04; B = 0.04 | | $k$ AB | 25 | 2.3 | -5 | | (3) |
| | | | 0.033 0.033 | | | " | 1.9 | -5 | | |
| | | | 0.025 0.025 | | | " | 1.1 | -5 | | |
| | | | 0.025 0.033 | | | " | 1.7 | -5 | | |
| | | | 0.020 0.025 | | | " | 1.0 | -5 | | |
| .3 | $C_2H_5I + AgNO_3$ | $CH_3OH$ | A = B = 0.025 | | $k$ AB | 24.5 | 7.3 | -5 | * | (2) |
| | | " | A = 0.025; B = 0.0125 | | $k$ AB | 25.0 | 7.5 | -5 | * | (4) |
| | | | 0.0125 0.0125 | | | " | 9.2 | -5 | | |
| | | | 0.025 0.025 | | | " | 1.24 | -4 | | |
| | | | 0.0125 0.025 | | | " | 1.40 | -4 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $C_2H_5I + AgNO_3$ *(continued)* | $CH_3OH + C_2H_5OH$ 25 vol % | 0.0125 | 0.0125 | | $k$ AB | 25.0 | 6.3 | -5 | | (4) |
| | | | | | | | " | 9.5 | -5 | | |
| | | | | | | | | 1.15 | -4 | | |
| | | 50 | 0.025 | 0.0125 | | " | " | 5.2 | -5 | | " |
| | | | 0.0125 | 0.0125 | | | " | 6.3 | -5 | | |
| | | | 0.025 | 0.025 | | | " | 7.8 | -5 | | |
| | | | 0.0125 | 0.025 | | | " | 9.0 | -5 | | |
| | | 75 | 0.0125 | 0.0125 | | " | " | 4.0 | -5 | | " |
| | | | 0.025 | 0.025 | | | " | 6.5 | -5 | | |
| | | | 0.0125 | 0.025 | | | " | 7.6 | -5 | | |
| | | $C_2H_5OH$ | 0.025 | 0.0125 | | " | " | 4.5 | -5 | * | (4) |
| | | | 0.0125 | 0.0125 | | | " | 4.6 | -5 | | |
| | | | 0.025 | 0.025 | | | " | 5.7 | -5 | | |
| | | | 0.0125 | 0.025 | | | " | 6.3 | -5 | | |
| | | " | A = B = 0.025 | | | $k$ AB | 24.5 | 3.7 | -5 | * | (2) |
| | | $CH_3CN$ | A = B = 0.1 | | | $k$ AB | 25 | 2.7 | -5 | | (3) |
| | | | 0.05 | | | | " | 1.75 | -5 | | |
| | | | 0.025 | | | | " | 1.35 | -5 | | |
| .3.1 | $C_2H_5I + \begin{cases} NO_3^- \ (LiNO_3) \ \ (B) \\ C_2H_5OH \end{cases}$ | | | $(a + b) = kA = k_1A + k_2AB;\ k = k_1 + k_2B$ | | | | | | * | (3a) |
| | $\longrightarrow \begin{cases} C_2H_5NO_3 + I^- & (a) \\ (C_2H_5)_2O + H^+ + I^- & (b) \end{cases}$ | $C_2H_5OH$ | A = 0.01: B = | | | | 25 | | | | |
| | | | 0 | | | | $k$ | 8.2 | -9 | | |
| | | | 0.06 | | | | | 9.8 | -9 | | |
| | | | 0.244 | | | | | 1.75 | -8 | | |
| | | | 0.488 | | | | | 2.49 | -8 | | |
| | | | | | | | $k_2$ | 3.3 | -8 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .3.1 | $C_2H_5I$ + $NO_3^-$ ($LiNO_3$) (B) | | | | | | 50 | | | | |
| | $C_2H_5OH$ | | 0 | | | | $k$ | 2.27 | −7 | * | ([3a]) |
| | $C_2H_5NO_3 + I^-$ *(a)* | | 0.06 | | | | | 3.00 | −7 | | |
| | $(C_2H_5)_2O + H^+ + I^-$ *(b)* | | 0.122 | | | | | 3.84 | −7 | | |
| | *(continued)* | | 0.224 | | | | | 6.67 | −7 | | |
| | | | 0.489 | | | | | 8.35 | −7 | | |
| | | | | | | | $k_2$ | 1.30 | −6 | | |
| | | $C_2H_5OH$ 96 % + $H_2O$ | A = 0.01; B = | | | " | 50 | | | | |
| | | | 0 | | | | $k$ | 3.67 | −7 | | |
| | | | 0.059 | | | | | 4.65 | −7 | | |
| | | | 0.144 | | | | | 5.06 | −7 | | |
| | | | 0.380 | | | | | 6.89 | −7 | | |
| | | | | | | | $k_2$ | 1.46 | −6 | | |
| | | $C_2H_5OH$ 36.9 % + $H_2O$ | A = 0.01; B = | | | " | 50 | | | | |
| | | | 0 | | | | $k$ | 2.34 | −6 | | |
| | | | 0.099 | | | | | 2.41 | −6 | | |
| | | | 0.248 | | | | | 2.70 | −6 | | |
| | | | 0.39 | | | | | 2.87 | −6 | | |
| | | | 0.497 | | | | | 3.29 | −6 | | |
| | | | | | | | $k_2$ | 1.46 | −6 | | |
| .4 | $C_3H_7I + AgNO_3$ | $CH_3OH$ | A = B = 0.025 | | | $k$ AB | 24.5 | 3.8 | −5 | * | ([2]) |
| | | $C_2H_5OH$ | " | | | " | " | 1.6 | −5 | | " |
| .5 | $(CH_3)_2CHI + AgNO_3$ | $C_2H_5OH$ | A = B = 0.005 | | | $k$ AB | 24.5 | 3.3 | −4 | | ([2]) |
| .6 | $C_4H_9I + AgNO_3$ | $CH_3OH$ | A = B = 0.025 | | | $k$ AB | 24.5 | 2.4 | −5 | * | ([2]) |
| | | $C_2H_5OH$ | " | | | " | " | 1.15 | −5 | | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .7 | $(CH_3)_2CHCH_2I + AgNO_3$ | $C_2H_5OH$ | A = B = 0.025 | | | $k$ AB | 24.5 | 2.3 | -5 | * | (2) |
| .8 | $(CH_3)_2CHCH_2CH_2I + AgNO_3$ | $C_2H_5OH$ | A = B = 0.025 | | | $k$ AB | 24.5 | 9.5 | -6 | * | (2) |
| .9 | $2C_6H_5CH_2Cl + Hg(NO_3)_2$ | 60 % dioxane + $H_2O$ | A = 0.025<br>B = 0.025 - 0.050 | $HNO_3$ | | $k$ AB | | | | | |
| | | | | | 0.013 - 0.029 | | 24.6 | 1.65 | -2 | * | (5) |
| | | | | | 0.085 | | " | 1.78 | -2 | | |
| .10 | $p$-$C_2H_5C_6H_4CH_2Br + NO_3^-$ | $(CH_3)_2CO$ | A = B = 0.025 | | | $k$ AB | 40 | 7.1 | -4 | * | (1) |
| .11 | $p$-$(CH_3)_3CC_6H_4CH_2Br + NO_3^-$ | $(CH_3)_2CO$ | A = B = 0.025 | | | $k$ AB | 40 | 6.8 | -4 | * | (1) |
| .12 | 2, 4 - $(NO_2)_2C_6H_3CH_2Br + NO_3^-$ | $(CH_3)_2CO$ | A = B = 0.025 | | | $k$ AB | 20 | 4.0 | -4 | * | (1) |
| | | | | | | | 40 | 3.3 | -3 | | |

## COMMENTS

**General.** The rate measured is $-dB/dt$. All reactions $RX + NO_3^- \longrightarrow RNO_3 + X^-$ in R'OH solvents are accompanied by solvolyses of $RNO_3$ according to $RNO_3 + R'OH \rightarrow ROR' + HNO_3$, resulting in mixed products. For reaction (.3) in $C_2H_5OH$, the solvolysis to $(C_2H_5)_2O$ accounts for 70 % of the reaction ([4]). (.3.1) Simultaneous exchange for $NO_3^-$ and solvolysis by $C_2H_5OH$ or $C_2H_5OH + H_2O$; $k$ refers to the total rate of production of $I^-$ by combined exchange and solvolysis, $k_2$ to the rate of exchange for $NO_3^-$. All $k$ converted from minutes to seconds. Data on solvolysis in $C_2H_5OH + H_2O$, and in the presence of $CH_3COO^-$ and of $(C_2H_5)_3N$, see 212.471. For reaction (.9), the fraction of $C_6H_5CH_2OH$ in the product varies, depending on the nature and amounts of nitrates added ($HNO_3$, $KNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$) in the range of 76 - 86 % of the total product. Reaction (.9) is complicated by formation of chloromercuribenzyl alcohol. $Hg(ClO_4)_2$ reacts faster than $Hg(NO_3)_2$. $HgCl_2$ accelerates the reaction in 60 % dioxane, but slows it down in 95 % dioxane. Data of ([2]) are valid for the given concentrations; $k$ increases with the square root of the concentration ([2]).

## LITERATURE

([1]) J.W.Baker, W.S.Nathan, *CSL* **1936**, 236. ([2]) K.A.Burke, F.G.Donnan, *CSL* **1904**, 555; *ZPC* 1909, **69**, 148. ([3]) F.G.Donnan, H.E.Potts, *CSL* **1910**, 1882. ([3a]) S.Eagle, J.C.Warner, *ACS* 1939, **61**, 488. ([4]) J.N.Pearce, O.M.Weigle, *ACJ* 1912, **48**, 243. ([5]) I.Roberts, L.P.Hammett, *ACS* 1937, **59**, 1063.

# EXCHANGE

## Halogen for $NH_2$ (or $NR_2$) group on aliphatic C

*Liquid phase*

Reaction type $RX + NH_3 \longrightarrow RNH_2 + HX$

(or $RX + 2\ NH_3 \longrightarrow RNH_2 + NH_4X$)

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $ClCH_2COONH_4 + NH_3$ | $H_2O$ | A = 0.05; B = 8.6 | | | $k$A | 39.9 | 1.50 | -4 | | * | ([1]) |
| | | | " 9.2 | | | " | " | 1.66 | -4 | | | |
| | | | " 9.1 | | | " | 50.0 | 4.0 | -4 | | | |
| | | | " 9.4 | | | " | " | 4.2 | -4 | | | |
| | | | " ~ 9 | | | $k$AB | 39.9 | 1.8 | -5 | | * | " |
| .2 | $ClCH_2CONHCH_2COONH_4 + NH_3$ (chloroacetylglycine) | $H_2O$ | A = 0.05; B = 9.3 | | | $k$A | 20.4 | 3.8 | -5 | | * | ([1]) |
| | | | " 9.1 | | | | 23.0 | 5.1 | -5 | | | |
| | | | " 9.3 | | | | 39.9 | 3.18 | -4 | | | |
| | | | " ~ 9 | | | $k$AB | 39.9 | 3.5 | -5 | | | " |
| .3 | $ClCH_2CONHCH_2CONHCH_2COONH_4 + NH_3$ (chloroacetylglycylglycine) | $H_2O$ | A = 0.05; B = 9.2 | | | $k$A | 18.1 | 3.6 | -5 | | * | ([1]) |
| | | | " 9.4 | | | | 19.1 | 4.3 | -5 | | | |
| | | | " 9.6 | | | | 39.9 | 4.32 | -4 | | | |
| | | | " ~ 9 | | | $k$AB | 39.9 | 4.6 | -5 | | * | " |



942151 O—51——25

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $ClCH_2CO(NHCH_2COO)_2NHCH_2COONH_4 + NH_3$ (chloroacetyldiglyeylglycine) | $H_2O$ | A = 0.05; B = 9.2 | | | $kA$ | 19.8 | 4.7 | -5 | | * | ([1]) |
| | | | " " | | | | 39.9 | 4.03 | -4 | | | |
| | | | " ~ 9 | | | $kAB$ | 39.9 | 4.3 | -5 | | * | " |
| .5 | $BrCH_2COONH_4 + NH_3$ | $H_2O$ | A = 0.05; B = 9.0 | | | $kA$ | 0.1 | 1.12 | -4 | | * | ([1]) |
| | | | " 9.2 | | | | 13.6 | 5.50 | -4 | | | |
| | | | " 9.2 | | | | 15.2 | 6.40 | -4 | | | |
| | | | " 9.0 | | | | 24.6 | 1.79 | -3 | | | |
| | | | " 9.2 | | | | 39.9 | 1.04 | -2 | | | |
| | | | " ~ 9 | | | $kAB$ | 39.9 | 1.1 | -3 | | * | " |
| .6 | $dl$ - $CH_3CHBrCOONH_4 + NH_3$ | $H_2O$ | A = 0.05; B = 9.1 | | | $kA$ | 21.0 | 5.0 | -5 | | * | ([1]) |
| | | | " 9.0 | | | | 28.2 | 1.07 | -4 | | | |
| | | | " 9.2 | | | | 39.9 | 4.00 | -4 | | | |
| | | | " ~ 9 | | | $kAB$ | 39.4 | 4.2 | -5 | | * | " |
| .7 | $dl$ - $(CH_3)_2CHCH_2CHBrCOONH_4 + NH_3$ | $H_2O$ | A = 0.05; B = 8.8 | | | $kA$ | 39.9 | 8.5 | -5 | | * | ([1]) |
| | | | " " | | | | 50.0 | 2.40 | -4 | | | |
| | | | " ~ 9 | | | $kAB$ | 39.9 | 9.7 | -6 | | * | " |
| .8 | $dl$ - $(CH_3)_2CHCH_2CHBrCONHCH_2COONH_4 + NH_3$ (bromoisocaproylglycine) | $H_2O$ | A = 0.05; B = 9.1 | | | $kA$ | 39.9 | 8.0 | -5 | | * | ([1]) |
| | | | " 9.0 | | | | 50.0 | 2.12 | -4 | | | |
| | | | " ~ 9 | | | $kAB$ | 39.9 | 8.6 | -6 | | * | " |
| .9 | $dl,dl$ - $(CH_3)_2CHCH_2CHBrCONHCH(CH_3)COONH_4 + NH_3$ (bromoisocaproylalanine) | $H_2O$ | A = 0.05; B = 8.9 | | | $kA$ | 39.9 | 7.0 | -5 | | * | ([1]) |
| | | | " " | | | | 50.0 | 2.0 | -4 | | | |
| | | | " ~ 9 | | | $kAB$ | 39.9 | 8.0 | -6 | | * | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .10 | $(C_6H_5)_3CBr + p\text{-}CH_3C_6H_4NH_2$ | $C_6H_6$ | A = 0.1; B = 0.03 - 0.2 | $C_5H_5N$ | 0.1 | | 25 | very fast | | | | (2) |
| .11 | $(C_6H_5)_3CBr + (C_6H_5)(CH_3)NH$ | $C_6H_6$ | A = 0.1; B = 0.03 - 0.2 | $C_5H_5N$ | 0.1 | $kAB^2$ | 25 | 5.0 | -4 | 6.6 (25 - 60°) | | (2) |

## COMMENTS

**(.1) - (.9)** First-order $k$ fairly constant owing to excess of $NH_3$. Second-order $k$ at 39.9°C converted to $sec^{-1}$ $(M/l)^{-1}$ units from original $k$ expressed in $sec^{-1}$ $atm^{-1}$ units, i.e. in terms of vapor pressure of $NH_3$ in atm. Original data (1) of $k$ at 39.9°C ($sec^{-1}$ $atm^{-1}$), $\Delta H_a$ and $\Delta S_a$:

| *Reaction* | $10^4 k$ | $\Delta H_a$ | $\Delta S_a$ |
|---|---|---|---|
| (.1) | 3.2 | 2.84 | -65.5 |
| (.2) | 6.0 | 2.73 | -64.5 |
| (.3) | 7.7 | 2.84 | -63.8 |
| (.4) | 7.3 | 2.69 | -64.4 |
| (.5) | (165) | 2.37 | -59.2 |
| (.6) | 7.0 | 2.60 | -65.0 |
| (.7) | 1.7 | 3.40 | -65.0 |
| (.8) | 1.5 | 3.20 | -66.0 |
| (.9) | 1.4 | 3.60 | -65.0 |

## LITERATURE

(1) A. F. Chadwick, E. Pacsu, *ACS* 1941, **63**, 2427. (2) C. G. Swain, *ACS* 1948, **70**, 1119.

# EXCHANGE

## Halogen for amine on aromatic C

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $ArX + NHR(NH_3) \rightarrow ArNR(ArNH_2) + HX$

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $p$-$CH_3COC_6H_4Br + C_5H_{10}NH$ | $C_6H_6$ | A = 0.05; B = 1.5 | | | $k$ AB | 99 | 8.6 | −8 | | | (1) |
| .2 | $p$-$NO_2C_6H_4Cl + C_5H_{10}NH$ | $C_6H_6$ | A = 0.05; B = 1.5 | | | $k$ AB | 99 | 1.1 | −6 | | | (1) |
| .3 | $p$-$NO_2C_6H_4Br + C_5H_{10}NH$ | $C_6H_6$ | A = 0.05; B = 1.5 | | | $k$ AB | 99 | 6.5 | −6 | | | (1) |
| .4 | $p$-$CNC_6H_4Br + C_5H_{10}NH$ | $C_6H_6$ | A = 0.05; B = 1.5 | | | $k$ AB | 99 | 1.2 | −7 | | | (1) |
| .5 | $p$-$CH_3SO_2C_6H_4Br + C_5H_{10}NH$ | $C_6H_6$ | A = 0.05; B = 1.5 | | | $k$ AB | 99 | 3.4 | −7 | | | (1) |
| .6 | $C_{19}H_{13}Cl + NH_3 \rightarrow C_{19}H_{13}NH_2 + HCl$ | $NH_3$ | A = 0.075; M = 0 − 0.2 | | $k_1A + k_2AM + k_3AX$ | | | | | | * | (2) |
| | (9-Ph-9-Cl-fluorene) | | | | | | 15.1 | | | | | |
| | | | | | | | $k_1$ | 9.7 | −6 | | | |
| | | | | | | | $k_2$ | 1.14 | −4 | | | |
| | | | | | | | 25.1 | | | | | |
| | | | | | | | $k_1$ | 2.22 | −5 | 14.3 | | |
| | | | | | | | $k_2$ | 2.65 | −4 | 14.4 | | |
| | | | | X = | | | | $k_3$ | | | | |
| | | | | NaCl | 0.05 − 0.2 | | 15.1 | 6.72 | −5 | | | |
| | | | | | | | 25.1 | 1.92 | −4 | 17.9 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $C_{19}H_{13}Cl + NH_3 \rightarrow C_{19}H_{13}NH_2 + HCl$ (9-Ph-9-Cl-fluorene) *(continued)* | | | $NaNO_3$ | 0.05 - 0.2 | | 15.1 | 1.13 | -4 | | | |
| | | | | | | | 25.1 | 3.34 | -4 | 15.6 | | |
| | | | | $NH_4NO_3$ | " | | 15.1 | 1.91 | -4 | | | |
| | | | | | | | 25.1 | 4.55 | -4 | 14.8 | | |

## COMMENTS

(.6) $k_3$ decreases somewhat with increasing X.

## LITERATURE

(1) J. F. Bunnet, A. Levitt, *ACS* 1948, 70, 2778. (2) P. M. Williamson, R. C. Anderson, G. W. Watt, *ACS* 1943, 65, 49; 1944, 66, 376.

# EXCHANGE

## Halogen for $S_2O_3^{--}$

*Liquid phase*

Reaction type $RX + S_2O_3^{--} \rightarrow RS_2O_3^{-} + X^{-}$

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, see at end of the table.

In compounds with two halogen atoms, if only one is exchanged ( reaction with 1 $S_2O_3^{--}$ ), it is the one written last. If the reaction equation involves 2 $S_2O_3^{--}$, both halogens are exchanged.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .1 | $CH_3Cl + S_2O_3^{--}$ | $H_2O$ | A ~ 0.02; B ~ 0.05 | $k$AB | 20.0 | 4.96 | -4 | | | | * | ([3a]) |
| | | | | | 24.9 | 9.09 | -4 | | | | | |
| | | | | | 30.0 | 1.62 | -3 | | | | | |
| | | | | | 40.0 | 4.71 | -3 | | | | | |
| | | | | | 49.6 | 1.32 | -2 | 20.5 | 1.0 | 12 | | |
| .2 | $CH_3Br + S_2O_3^{--}$ | $H_2O$ | A ~ 0.02; B ~ 0.05 | $k$AB | 0.1 | 1.93 | -3 | | | | * | ([3a]) |
| | | | | | 4.8 | 3.36 | -3 | | | | | |
| | | | | | 9.2 | 6.00 | -3 | | | | | |
| | | | | | 15.5 | 1.30 | -2 | | | | | |
| | | | | | 20.0 | 2.19 | -2 | | | | | |
| | | | | | 25.1 | 3.77 | -2 | 19.5 | 6.8 | 12 | | |
| .3 | $CH_3I + S_2O_3^{--}$ | $H_2O$ | A ~ 0.02; B ~ 0.05 | $k$AB | 9.2 | 4.83 | -3 | | | | * | ([3a]) |
| | | | | | 12.9 | 7.56 | -3 | | | | | |
| | | | | | 19.2 | 1.56 | -2 | | | | | |
| | | | | | 25.5 | 3.15 | -2 | 18.9 | 2.0 | 12 | | |
| .4 | $C_2H_5Br + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$AB | 25 | 5.2 | -4 | | | | | ([4]) |
| | | | | | 50 | 8.3 | -3 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $C_2H_5Br + S_2O_3^{--}$ *(continued)* | Et50A | ~ 0.1 | $k$AB | 12.5 | 2.43 | -4 | | * | (1) |
| | | | | | 25.0 | 9.53 | -4 | | | |
| | | | | | 37.5 | 3.33 | -3 | 18.5 | | |
| .5 | $C_2H_5I + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$AB | 25 | 8.3 | -4 | | * | (4) |
| | | | | | 35 | 2.8 | -3 | | | |
| | | $H_2O$ | 0.015 | $k$AB | 25.0 | 1.23 | -3 | | * | (3) |
| | | | | | 36.2 | 4.25 | -3 | | | |
| | | | | | 44.5 | 1.21 | -2 | | | |
| | | | | | 51.6 | 2.55 | -2 | | | |
| | | | | | 55.6 | 3.59 | -2 | 21.4 | | |
| .6 | $CH_2ClCH_2Br + S_2O_3^{--}$ | EtW 3 | B>A | $k$AB | 40 | 8.3 | -6 | | | (4) |
| | | | | | 50 | 2.5 | -5 | | | |
| .7 | $CH_2ClCH_2I + S_2O_3^{--}$ | EtW 3 | B>A | $k$AB | 40 | 2.3 | -5 | | | (4) |
| | | | | | 50 | 6.7 | -5 | | | |
| .8 | $CH_2BrCH_2Br + S_2O_3^{--}$ | EtW 3 | B>A | $k$AB | 40 | 2.8 | -3 | | | (4) |
| | | | | | 50 | 8.2 | -3 | | | |
| .9 | $CH_2BrCH_2I + 2\ S_2O_3^{--}$ | EtW 2 | 0.01 | $k$AB | 15 | 3.5 | -3 | | * | (4) |
| | | | | | 25 | 9.2 | -3 | | | |
| .10 | $CH_2ICH_2I + 2\ S_2O_3^{--}$ | EtW 2 | 0.01 | $k$AB | 15 | 5.7 | -3 | | * | (4) |
| | | | | | 25 | 1.7 | -2 | | | |
| .11 | $C_3H_7Br + S_2O_3^{--}$ | Et50A | ~ 0.1 | $k$AB | 12.5 | 1.27 | -4 | | * | (1) |
| | | | | | 25.0 | 4.74 | -4 | | | |
| | | | | | 37.5 | 1.63 | -3 | 18.0 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .12 | $(CH_3)_2CHBr + S_2O_3^{--}$ | Et50A | ~ 0.1 | $k$ AB | 12.5 | 6.77 | -6 | | * | ([1]) |
| | | | | | 25.0 | 2.94 | -5 | | | |
| | | | | | 37.5 | 1.18 | -4 | 20.1 | | |
| .13 | $C_3H_7I + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$ AB | 35 | 9.3 | -4 | | | ([4]) |
| .14 | $(CH_3)_2CHI + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$ AB | 35 | 5.7 | -6 | | | ([4]) |
| .15 | $CH_2{:}CHCH_2I + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$ AB | 15 | 2.3 | -2 | | | ([4]) |
| | | | | | 25 | 6.0 | -2 | | | |
| .16 | $(CH_3)_2CHCH_2Br + S_2O_3^{--}$ | Et50 | ~ 0.01 | $k$ AB | 12.5 | 4.59 | -6 | | * | ([2]) |
| | | | | | 25.0 | 2.02 | -5 | | | |
| | | | | | 37.5 | 7.60 | -5 | | | |
| | | | | | 50.0 | 2.60 | -4 | 19.7 | | |
| | **Acids, Esters, Ethers** | | | | | | | | | |
| .17 | $ClCOOC_2H_5 + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$ AB | 35 | 1.7 | -2 | | | ([4]) |
| .18 | $CH_2ClCOO^- + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$ AB | 25 | 7.0 | -5 | | | ([4]) |
| | | | | | 50 | 6.6 | -4 | | | |
| .19 | $CH_2ClCOOCH_3 + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$ AB | 25 | 9.8 | -4 | | | ([4]) |
| | | | | | 35 | 2.7 | -3 | | | |
| .20 | $CH_2ClCOOC_2H_5 + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$ AB | 25 | 1.0 | -3 | | | ([4]) |
| | | | | | 35 | 2.9 | -3 | | | |
| .21 | $CH_2BrCOO^- + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$ AB | 25 | 5.2 | -3 | | | ([4]) |
| | | | | | 35 | 1.1 | -2 | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .22 | $CH_2BrCOOCH_3 + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$AB | 15 | 3.5 | -2 | | | (4) |
| | | | | | 25 | 9.7 | -2 | | | |
| .23 | $CH_2BrCOOC_2H_5 + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$AB | 15 | 3.9 | -2 | | | (4) |
| | | | | | 25 | 1.1 | -1 | | | |
| .24 | $CH_2ICOOC_2H_5 + S_2O_3^{--}$ | $H_2O$ | 0.01 | $k$AB | 15 | 4.25 | -2 | | | (4) |
| | | | | | 25 | 1.2 | -1 | | | |
| .25 | $CH_3CHBrCOOC_2H_5 + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 25 | 6.2 | -4 | | | (4) |
| | | | | | 35 | 1.4 | -3 | | | |
| .26 | $C_2H_5CHBrCOOC_2H_5 + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | 3.7 | -4 | | | (4) |
| .27 | $(CH_3)_2CBrCOOC_2H_5 + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | slow | | | | (4) |
| .28 | $CH_2ClCOCH_3 + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 25 | 6.3 | -3 | | | (4) |
| | | | | | 35 | 1.75 | -2 | | | |
| .29 | $CH_2ClCH<\begin{smallmatrix}O\\ \vert\\ CH_2\end{smallmatrix} + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | 1.7 | -3 | | | |
| | **Aryl-substituted alkyl halide** | | | | | | | | | |
| .30 | $C_6H_5CH_2Cl + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | 2.8 | -3 | | | (4) |
| .31 | $o\text{-}NO_2C_6H_4CH_2Cl + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | 2.8 | -3 | | | (4) |
| .32 | $m\text{-}NO_2C_6H_4CH_2Cl + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | 3.2 | -3 | | | (4) |
| .33 | $p\text{-}NO_2C_6H_4CH_2Cl + S_2O_3^{--}$ | EtW 3 | 0.01 | $k$AB | 35 | 5.0 | -3 | | | (4) |

## SOLVENTS

| | |
|---|---|
| EtW 2 | $C_2H_5OH + H_2O$; $C_2H_5OH/H_2O = 5/2$ ( vol ). |
| EtW 3 | " " " " = 5/3 " |
| Et50 | $H_2O + C_2H_5OH$ 50 % |
| Et50A | $H_2 + C_2H_5OH$ 50 %; $CH_3COONa$ 0.020 *M*. |

## SUPPLEMENTARY TABLE

**Heat and Entropy of Activation** (1) (2)

$\Delta H_a$ (kcal/mole) and $\Delta S_a$ (cal/mole/degree) referred to $C_2H_5Br$ as zero.
For $C_2H_5Br$, $\Delta S_a = -12.3$.

| | Reaction | Solvent | $\Delta H_a$ | $\Delta S_a$ |
|---|---|---|---|---|
| (.2) | $CH_3Br + S_2O_3^{--}$ | Et50 | - 2.9 | - 0.6 |
| (.11) | $C_3H_7Br + S_2O_3^{--}$ | Et50A | - 0.5 | - 3.0 |
| (.12) | $(CH_3)_2CHBr + S_2O_3^{--}$ | Et50A | 1.6 | - 0.9 |
| (.16) | $(CH_3)_2CHCH_2Br + S_2O_3^{--}$ | Et50 | 1.1 | - 3.4 |

## COMMENTS

(.1) (.2) (.3) New data of ([3a]) given in preference to the markedly lower, old data of $k$ of ([4]). Hydrolysis of A is negligible. (.4) In Et5OA ([1]), simultaneous solvolysis by $CH_3COO^-$ negligible. (.5) $k$ of ([3]), more reliable, are about 50 % higher than $k$ of ([4]) at the same temperatures; $k$ of ([3]) are initial values, the second-order $k$ falling off somewhat with the progress of the reaction, in conformity with a true rate law $k_1A + k_2AB$, with $k_1 \ll k_2$. (.9) (.10) Original $k$, halved to apply to one halogen, have been doubled. (.11) Stimultaneous solvolysis by $CH_3COO^-$ negligible (.12) Stimultaneous solvolysis *not* negligible; $k$ corrected. At 25.0 and 37.5°C, $k$ ( solvolysis ) = $3.4 \times 10^{-7}$ and $1.7 \times 10^{-6}$, respectively.

## LITERATURE

([1]) F.J.Crowell, L.P.Hammett, *ACS* 1948, **70**, 3444. ([2]) P.M.Dunbar, L.P.Hammett, *ACS* 1950, **72**, 109. ([3]) E.A.Moelwyn-Hughes, *CSL* 1933, 1576. ([4]) A.Slator, D.F.Twiss, *CSL* 1909, **95**, 93; A.Slator, *CSL*, 1904, **85**, 1286.

# EXCHANGE

## Halogen for halogen on aliphatic carbon

Reaction type $RX_1 + X_2^- \rightarrow RX'_2 + X_1^-$

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, see at the end of the table.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3Br + I^-$ | $H_2O$ | 0.035-0.060 | $k$ AB | 0.5 | 4.5 | −5 | | | | | (6) |
| | | | | | 20.4 | 4.36 | −4 | | | | | |
| | | | | | 25.0 | 7.02 | −4 | | | | | |
| | | | | | 35.5 | 2.00 | −3 | | | | | |
| | | | | | 50.3 | 7.70 | −3 | | | | | |
| | | | | | 66.9 | 3.12 | −2 | 18.3 | 1.7 | 10 | | |
| | | $CH_3OH$ | | $k$ AB | 0.0 | 5.3 | −5 | | | | | (7) |
| | | | | | 15.5 | 3.53 | −4 | | | | | |
| | | | | | 24.8 | 9.84 | −4 | | | | | |
| | | | | | 34.6 | 2.43 | −3 | | | | | |
| | | | | | 44.6 | 6.35 | −3 | 18.2 | 2.3 | 10 | | |
| .2 | $CH_3I + Br^-$ | $CH_3OH$ | | $k$ AB | 0.0 | 2.94 | −6 | | | | | (7) |
| | | | | | 20.4 | 4.54 | −5 | | | | | |
| | | | | | 30.2 | 1.38 | −4 | | | | | |
| | | | | | 40.3 | 4.54 | −4 | | | | | |
| | | | | | 49.1 | 1.21 | −3 | 21.4 | 3.9 | 11 | | |
| .3 | $C_2H_5Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 2.8 | −5 | | | | | (4) |
| | | | | | 60 | 5.4 | −5 | 14.2 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $CH_3OCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 0 | ~ 5.4 | -5 | | | | | (5) |
| | | | | | 10 | ~ 1.7 | -4 | | | | | |
| .5 | $CNCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 10 | 6.2 | -4 | | | | | (5) |
| | | | | | 20 | 1.96 | -3 | 18.8 | | | | |
| .6 | $NH_2COCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 25 | 1.0 | -4 | | | | | (5) |
| | | | | | 30 | 1.66 | -4 | | | | | |
| | | | | | 50 | 1.10 | -3 | 18.3 | | | | |
| .7 | $C_3H_7Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.2 | -5 | | | | | (4) |
| | | | | | 60 | 2.0 | -5 | 18.8 | | | | |
| .8 | $(CH_3)_2CHCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 4.1 | -7 | | | | | (4) |
| .9 | $C_2H_5OOCCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 25 | 2.6 | -5 | | | | | (4) (5) |
| .10 | $CH_3COCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 0 | 2.1 | -3 | | | | | (5) |
| | | | | | 10 | 7.9 | -3 | 19.7 | | | | |
| .11 | $CH_3COOCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 20 | 1.6 | -4 | | | | | |
| | | | | | 30 | 2.7 | -4 | 18.3 | | | | |
| .12 | $C_4H_9Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.1 | -5 | | | | | (4) (5) |
| | | | | | 60 | 2.8 | -5 | 19.7 | | | | |
| .13 | $C_2H_5CH(CH_3)Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 6.1 | -7 | | | | | (4) |
| .14 | $C_2H_5OOCCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 25 | 1.76 | -3 | | | | | (4) (5) |
| | | | | | 30 | 2.90 | -3 | 17.8 | | | | |
| .15 | $(CH_3)_3CCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 5.0 | -7 | | | | | (4) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .16 | $C_5H_{11}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.5 | −5 | | | | | (4) |
| | | | | | 60 | 3.5 | −5 | 18.3 | | | | |
| .17 | $(CH_3)_2CHCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 1.9 | −5 | | | | | (4) |
| .18 | $C_3H_7CH(CH_3)Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 1.33 | −6 | | | | | (4) |
| .19 | $C_6H_{13}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.45 | −5 | | | | | (4) |
| | | | | | 60 | 3.5 | −5 | 18.8 | | | | |
| .20 | $C_4H_9CH(CH_3)Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 2.1 | −6 | | | | | (4) |
| .21 | $(C_3H_7)(CH_3)_2CCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 8.0 | −7 | | | | | (4) |
| .22 | $C_7H_{15}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.4 | −5 | | | | | (4) |
| | | | | | 60 | 3.4 | −5 | 18.8 | | | | |
| .23 | $(C_2H_5OOC)_2CHCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 0 | 3.6 | −3 | | | | | (8) |
| | | | | | 10 | 6.6 | −3 | | | | | |
| .24 | $C_8H_{17}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.5 | −5 | | | | | (4) |
| | | | | | 60 | 3.7 | −5 | 19.2 | | | | |
| .25 | $C_6H_{13}CH(CH_3)Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 60 | 7.2 | −7 | | | | | (4) |
| .26 | $C_{12}H_{25}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.3 | −5 | | | | | (4) |
| | | | | | 60 | 2.8 | −5 | 17.1 | | | | |
| .27 | $C_{14}H_{29}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.1 | −5 | | | | | (4) |
| | | | | | 60 | 2.7 | −5 | 19.2 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .28 | $C_{16}H_{33}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.0 | −5 | | | | | (4) |
| | | | | | 60 | 2.5 | −5 | 19.2 | | | | |
| .29 | $C_{30}H_{61}Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 50 | 1.0 | −5 | | | | | (4) |
| | | | | | 60 | 2.46 | −5 | 18.8 | | | | |
| **Aryl-substituted aliphatic halide** | | | | | | | | | | | | |
| .30 | $C_6H_5CH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 25 | 2.18 | −4 | | | | | (4) (5) |
| | | | | | 30 | 3.64 | −4 | | | | | |
| | | | | | 50 | 2.19 | −3 | 18.3 | | | | |
| | | An 50 | | $k$ AB | 0.1 | 3.7 | −5 | | | | | |
| | | | | | 20 | 3.7 | −4 | 18.3 | | | | (3) |
| .31 | $C_6H_5CH_2CH_2Cl + I^-$ | An 50 | | $k$ AB | 75 | 2.4 | −4 | | | | | (2) |
| .32 | $p$-$CH_3OC_6H_4CH_2CH_2Cl + I^-$ | An 50 | | $k$ AB | 75 | 2.9 | −4 | | | | | (2) |
| .33 | $(C_6H_5)_3CCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 0 | 2.28 | −3 | | | | | (5) |
| .34 | $C_6H_5COCl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 0 | ~4.4 | −5 | | | | | (5) |
| .35 | $C_6H_5COCH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | − 10 | 1.64 | −3 | | | | | (4) (5) |
| | | | | | 0 | 6.2 | −3 | | | | | |
| .36 | $C_6H_5COCH_2CH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 25 | 2.35 | −4 | | | | | (5) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .37 | $C_6H_4NHC(CH_2Cl):N + I^-$ | $(CH_3)_2CO$ | A = 0.1; B = 0.02 | $k$ AB | 25 | 8.2 | −3 | | | | * | (8) |
| | | | 0.01 0.03 | | " | 4.15 | −2 | | | | | |
| | | | 0.005 " | | " | 6.5 | −2 | | | | | |
| | | | " 0.01 | | " | 7.2 | −2 | | | | | |
| | | | " 0.02 | | " | 1.08 | −1 | | | | | |
| .38 | $C_6H_4NHC(CH_2CH_2Cl):N + I^-$ | $(CH_3)_2CO$ | A = 0.05; B = 0.02 | $k$ AB | 25 | 1.22 | −2 | | | | * | (8) |
| | | | 0.02 " | | " | 2.54 | −2 | | | | | |
| | | | " 0.01 | | " | 3.80 | −2 | | | | | |
| | | | 0.01 0.026 | | " | 4.55 | −2 | | | | | |
| .39 | $C_6H_4NHC(CH_2CH_2CH_2Cl):N + I^-$ | $(CH_3)_2CO$ | A = 0.03; B = 0.016 | $k$ AB | 25 | 1.26 | −2 | | | | * | (8) |
| | | | 0.02 0.02 | | " | 4.9 | −2 | | | | | |
| | | | 0.025 0.01 | | " | 5.7 | −2 | | | | | |
| | | | 0.01 0.02 | | " | 9.3 | −2 | | | | | |
| .40 | $C_6H_4NHC[CH(CH_3)CH_2Cl]:N + I^-$ | $(CH_3)_2CO$ | A = 0.02; B = 0.02 | $k$ AB | 25 | 6.5 | −2 | | | | * | (8) |
| | | | 0.025 0.01 | | " | 2.42 | −1 | | | | | |
| | | | 0.01 0.02 | | " | 4.25 | −1 | | | | | |
| .41 | $C_6H_4N(CH_3)C(CH_2Cl):N + I^-$ | $(CH_3)_2CO$ | A = 0.02; B = 0.02 | $k$ AB | 25 | 7.0 | −3 | | | | * | (8) |
| | | | 0.025 0.01 | | " | 2.50 | −2 | | | | | |
| | | | 0.01 0.02 | | " | 6.95 | −2 | | | | | |
| .42 | $C_6H_4N(CH_3)C(CH_2CH_2Cl):N + I^-$ | $(CH_3)_2CO$ | A = 0.038; B = 0.02 | $k$ AB | 25 | 1.2 | −2 | | | | * | (8) |
| | | | 0.029 " | | " | 1.65 | −2 | | | | | |
| | | | 0.025 0.01 | | " | 1.50 | −1 | | | | | |
| | | | 0.005 0.02 | | " | 2.30 | −1 | | | | | |
| .43 | $o\text{-}NO_2C_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 3.6 | −4 | | | | | (3) |
| | | | | | 20 | 3.16 | −4 | 17.4 | | | | |



942151 O—51——26

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .44 | $m$-$NO_2C_6H_4CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 0.1 | 1.35 | −4 | | | | | (3) |
| | | | | | 20 | 1.33 | −2 | 18.4 | | | | |
| .45 | $p$-$NO_2C_6H_4CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 0.1 | 2.5 | −4 | | | | | (3) |
| | | | | | 20 | 2.26 | −3 | 17.6 | | | | |
| .46 | $p$-$NO_2C_6H_4CH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 75 | 1.14 | −3 | | | | | (2) |
| .47 | $o$-$FC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 1.25 | −4 | | | | | (3) |
| | | | | | 20 | 1.08 | −3 | 17.2 | | | | |
| .48 | $m$-$FC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 5.1 | −5 | | | | | (3) |
| | | | | | 20 | 5.12 | −4 | | | | | |
| .49 | $p$-$FC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 5.7 | −5 | | | | | (3) |
| | | | | | 20 | 5.3 | −4 | 17.8 | | | | |
| .50 | $p$-$FC_6H_4CH_2CH_2Cl + I^-$ | An 50 | | $k$ AB | 75 | 4.3 | −4 | | | | | (2) |
| .51 | $o$-$ClC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 1.76 | −4 | | | | | (3) |
| | | | | | 20 | 1.45 | −3 | 16.9 | | | | |
| | | $(CH_3)_2CO$ | A = 0.2; B = 0.04 | $k$ AB | 25 | 7.5 | −4 | | | | | (4) |
| | | | | | 30 | 1.22 | −3 | 17.6 | | | | |
| .52 | $m$-$ClC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 6.5 | −5 | | | | | (3) |
| | | | | | 20 | 6.0 | −4 | 17.7 | | | | |
| .53 | $p$-$ClC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 8.1 | −5 | | | | | (3) |
| | | | | | 20 | 7.9 | −4 | 18.0 | | | | |
| .54 | $p$-$ClC_6H_4CH_2CH_2Cl + I^-$ | An 50 | | $k$ AB | 75 | 4.55 | −4 | | | | | (2) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .55 | $o$-$BrC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 1.57 | −4 | | | | | (3) |
| | | | | | 20 | 1.46 | −3 | 17.8 | | | | |
| .56 | $m$-$BrC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 7.2 | −5 | | | | | (3) |
| | | | | | 20 | 6.85 | −4 | 18.0 | | | | |
| .57 | $p$-$BrC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 1.39 | −4 | | | | | (3) |
| | | | | | 20 | 8.7 | −4 | 18.7 | | | | |
| .58 | $p$-$BrC_6H_4CH_2CH_2Cl + I^-$ | An 50 | | $k$ AB | 75 | 4.52 | −4 | | | | | (2) |
| .59 | $o$-$IC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 1.74 | −4 | | | | | (3) |
| | | | | | 20 | 1.53 | −3 | 17.4 | | | | |
| .60 | $m$-$IC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 6.7 | −5 | | | | | (3) |
| | | | | | 20 | 6.5 | −4 | 18.1 | | | | |
| .61 | $p$-$IC_6H_4CH_2Cl + I^-$ | An 50 | | $k$ AB | 0.1 | 8.2 | −5 | | | | | (3) |
| | | | | | 20 | 8.25 | −4 | 18.4 | | | | |
| .62 | $p$-$IC_6H_4CH_2CH_2Cl + I^-$ | An 50 | | $k$ AB | 75 | 3.90 | −4 | | | | | (2) |
| | **Arylthio-substituted aliphatic halide** | | | | | | | | | | | |
| .63 | $C_6H_5SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 55 | 2.5 | −5 | | | | | (1) |
| .64 | $p$-$CH_3C_6H_4SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 55 | 2.1 | −5 | | | | | (1) |
| | | | | | 75 | 1.21 | −4 | 20.3 | | | | |
| .65 | $p$-$CH_3OC_6H_4SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 75 | 1.2 | −4 | | | | | (1) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .66 | $p$-$ClC_6H_4SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 55 | 5.5 | −5 | | | | | ([1]) |
| | | | | | 75 | 3.5 | −4 | 21.0 | | | | |
| .67 | 2, 5-$Cl_2C_6H_3SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 55 | 5.2 | −5 | | | | | ([1]) |
| | | | | | 75 | 3.1 | −4 | 20.3 | | | | |
| .68 | $p$-$BrC_6H_4SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 55 | 4.2 | −5 | | | | | ([1]) |
| | | | | | 75 | 2.65 | −4 | 21.1 | | | | |
| .69 | $p$-$IC_6H_4SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 55 | 3.2 | −5 | | | | | ([1]) |
| | | | | | 75 | 2.2 | −4 | 21.9 | | | | |
| .70 | $\beta$-$C_{10}H_7SCH_2CH_2Cl + I^-$ | $(CH_3)_2CO$ | | $k$ AB | 75 | 1.85 | −4 | | | | | ([1]) |

## SOLVENTS

An 50 $H_2O + (CH_3)_2CO$ 50 vol %

## COMMENTS

(.37)-(.42) Selected values. Addition of $H_2O$ or $C_6H_5NO_2$ lowers *k*, addition of $C_6H_6$ raises *k*.

## LITERATURE

(1) G. Baddeley, G. Mc. Bennett, *CSL* 1933, 261.

(2) G. Baddeley, G. Mc. Bennett, *CSL* 1935. 1819.

(3) G. Mc. Bennett, B. Jones, *CSL* 1935, 1815.

(4) J. B. Conant, R. E. Hussey, *ACS* 1925, 47, 476.

(5) J. B. Conant, W. R. Kirner, R. E. Hussey, *ACS* 1925, 47, 488.

(6) E. A. Moelwyn-Hughes, *CSL* 1938, 779.

(7) E. A. Moelwyn-Hughes, *TFS* 1939, 35, 368.

(8) H. Skolnik, A. R. Day, J. C. Miller, *ACS* 1943, 65, 1858.

# EXCHANGE

## Halogen for halogen on aromatic and hydroaromatic carbon

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $ArX + X'^{-} \longrightarrow ArX' + X^{-}$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^{o} \times 10^{n}$ | | $E$ | $A = A^{o} \times 10^{n}$ | | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^{o}$ | $n$ | | $A^{o}$ | $n$ | |
| .1 | *cyclo*-$C_6H_{11}Cl$ + KI | $(CH_3)_2CO$ | A = 0.2<br>B = 0.04 | $k$ AB | 60 | < 2.8 | −8 | | | | (2) |
| .2 | *p*-$NO_2C_6H_4Cl$ + LiBr | 90 % $(CH_3)_2CO$ | | $k$ AB | 30 | 1.35 | −4 | | | | (1) |
| | | | | | 50 | 6.7 | −4 | 15.6 | 2.5 | 7 | |
| .3 | *p*-$NO_2C_6H_4Br$ + LiCl | 90 % $(CH_3)_2CO$ | | $k$ AB | 30 | 2.14 | −3 | | | | (1) |
| | | | | | 50 | 1.32 | −2 | 17.9 | 1.6 | 10 | |

## LITERATURE

(1) T. A. Bither, J. M. Sturtevant, H. C. Thomas, *ACS* 1945, **67**, 1562.

(2) J. B. Conant, R. E. Hussey, *ACS* 1925, **47**, 476.

# EXCHANGE

## Halogen for $ClO_4^-$

*Liquid phase*

Amounts are in M/l.
Rates in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3I + AgClO_4 \rightarrow CH_3ClO_4 + AgI$ | $(C_2H_5)_2O$ | A = B ~ 0.005 – 0.2 | $k$ AB | 15 | 5.0 | –4 | |
| | | | | | 25 | 9.2 | –4 | |
| | | $CH_3COOH$ | 0.04 – 0.08 | $k$ $AB^{3/2}$ | 15 | 1.8 | –4 | |
| | | | | | 25 | 3.8 | –4 | 12.7 |
| | | $(CH_3)_2CO$ | " | " | 25 | 1.8 | –4 | |
| | | $C_2H_5OH$ | " | " | 15 | 3.3 | –4 | |
| | | | | | 25 | 7.0 | –4 | 13.0 |
| | | $CH_3COOC_2H_5$ | " | " | 25 | 1.1 | –3 | |
| | | $H_2O + \underbrace{CH_2OCH_2O}$ 50 % | " | " | 15 | 1.8 | –4 | |
| | | | | | 25 | 4.0 | –4 | 13.3 |
| | | $H_2O + C_2H_5OH$ 50 % | A = B ~ 0.08 – 0.16 | " | 15 | 2.5 | –4 | |
| | | | | | 25 | 5.0 | –4 | 11.4 |
| | | $C_6H_6$ | " | " | 25 | 4.1 | –5 | |
| | | | | | 35 | 9.0 | –5 | 13.9 |

### COMMENTS

At low concentrations of $AgClO_4$, the $k$ $AB^{3/2}$ reaction rate law becomes pseudo-bimolecular, $k'$ AB ($k'$ proportional to $B^{1/2}$).

### LITERATURE

M. F. Redies, T. Iredale, *JPC* 1944, 48, 224.

# EXCHANGE

## Halogen for hydrogen in cyanogen halide

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $CNBr + 2\ HI \rightarrow HCN + HBr + I_2$ | $CCl_4$ | $10^3A = 35.5$; $10^3B = 0.3$ | $k$AB | 25 | 1.3 | -1 |
| | $(CNBr + HI \rightarrow CNI + HBr)$ | | 5.0 2.5 | | " | 4.1 | -1 |
| | | | 5.0 1.3 | | " | 2.0 | -1 |
| | | | 5.0 0.6 | | " | 1.1 | -1 |
| | | | 2.5 2.5 | | " | 1.3 | -1 |
| .2 | $CNI + HI \rightarrow HCN + I_2$ | $CCl_4$ | $10^3A = 0.6$; $10^3B = 1.7$ | $k$AB | 25 | 2.1 | +4 |
| | | | 0.6 0.8 | | " | 2.5 | +4 |
| | | | 1.2 0.8 | | " | 2.6 | +4 |
| | | | 1.2 0.4 | | " | 1.7 | +4 |
| | | | 0.6 0.4 | | " | 7.0 | +3 |
| | | | 5.7 0.2 | | " | 4.0 | +3 |

## COMMENTS

Reaction (.1) is assumed to proceed over the rate-determining slow step $CNBr + HI \rightarrow CNI$, followed by the rapid step (.2). The scattering of the second-order $k$ is attributed to experimental difficulties. Mean values of $k$ are given as (.1) $k = 2.0 \times 10^{-1}$, (.2) $k = 1.6 \times 10^4$. The reaction CNCl + HI is substantially slower than CNBr + HI.

## LITERATURE

R. B. Mooney, H. G. Reid, *CSL* **1933**, 1318.

# EXCHANGE

## Halogen for $NH_2$ (or $NR_2$) group in cyanogen halide

*Liquid phase*

Reaction type $CNX + NR_3 \rightarrow CNNR_2 + RX$

(or $CNX + 2\ NR_3 \rightarrow CNNR_2 + NR_3RX$)

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Ionic strength $\mu$ | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $CNBr + NH_3$ | $H_2O$ | 0.2 | $k$AB | 10 | 3.25 | -3 | 17.5 |
| .2 | $CNBr + CH_3NH_2$ | $H_2O$ | 1.0 | $k$AB | 10 | 2.22 | 0 | 14.5 |
| .3 | $CNBr + C_2H_5NH_2$ | $H_2O$ | 1.0 | $k$AB | 10 | 1.08 | 0 | 14.3 |
| .4 | $CNBr + (C_2H_4OH)_3N$ | $H_2O$ | 1.0 | $k$AB | 10 | 3.93 | -2 | 14.9 |
| .5 | $CNI + NH_3$ | $H_2O$ | 3.0 | $k$AB | 10 | 7.60 | -6 | 19.6 |
| .6 | $CNI + CH_3NH_2$ | $H_2O$ | 1.0 | $k$AB | 10 | 8.35 | -3 | 17.1 |
| .7 | $CNI + C_2H_5NH_2$ | $H_2O$ | 1.0 | $k$AB | 10 | 4.30 | -3 | 17.2 |
| .8 | $CNI + (CH_3)_2NH$ | $H_2O$ | 1.0 | $k$AB | 10 | 2.17 | -1 | 17.0 |
| .9 | $CNI + (C_2H_5)_2NH$ | $H_2O$ | 1.0 | $k$AB | 10 | 6.38 | -2 | 16.4 |
| .10 | $CNI + (CH_3)_3N$ | $H_2O$ | 1.0 | $k$AB | 10 | 2.54 | -1 | 17.6 |
| .11 | $CNI + (C_2H_5)_3N$ | $H_2O$ | 1.0 | $k$AB | 10 | 4.50 | -2 | 16.7 |
| .12 | $CNI + (C_2H_4OH)_3N$ | $H_2O$ | 1.0 | $k$AB | 10 | 4.35 | -5 | 18.5 |

## LITERATURE

R. O. Griffith, R. S. Jobin, A. McKeown, *TFS* 1938, **34**, 316.

# COORDINATIVE EXCHANGE

## Halogen - water in VIII th - group complex.

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|
| .1 | $[Co(NH_3)_5Cl]^{++} + H_2O \rightarrow [Co(NH_3)_5(H_2O)^{+++} + Cl^-$ | $H_2O$ | 0.007 - 0.015 | $k$ A | 1.7 | -6 | 23.7 |
| .2 | $[Co(NH_3)_5(H_2O)]^{+++} + Cl^- \rightarrow [Co(NH_3)_5Cl]^{++} + H_2O$ | $H_2O$ | 0.007 - 0.015 | $k$ AB | 7.2 | -6 | |

## COMMENTS

(.1)(.2) $k$ identical for the chloride, nitrate, and perchlorate, depends on the anion but not on the cation; perchlorate. Salt effect, positive except for the is usually less than 1 %.

## LITERATURE

F. J. Garrick, *TFS* 1937, 33, 486. A. B. Lamb, J. W. Marden, *ACS* 1911, 33, 1882.

# ELIMINATION

## of $H^+$ from a C - N bond

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3NO_2 + H_2O \rightarrow CH_2{:}NO_2^- + H_3O^+$ | $H_2O$; buffers | ~ 0.001 | pH | 6.1 | $k$ A | 25 | 1.20 | -4 | | | | | ([5]) ([9]) |
| | | | | | 7.0 | | " | 1.65 | -4 | | | | | |
| | | | | | 8.0 | | " | 2.50 | -4 | | | | | |
| | | | | | 8.9 | | " | 3.00 | -4 | | | | | |
| | | $H_2O$ | A ~ 0.15 - 0.7 | $H_2SO_4$ | ~ 0.15 | $k$ AB | 70 | 1.2 | -7 | | | | * | ([8]) |
| | | | | $Br_2$ | ~ 0.03 | | | | | 22 | | | | ([1]) |
| .2 | $CH_3NO_2 + D_2O \rightarrow CH_2{:}NO_2^- + HD_2O^+$ | $D_2O$ | A ~ 0.15 - 0.7 | $H_2SO_4$ | ~ 0.15 | $k$ AB | 70 | 7.3 | -8 | | | | * | ([8]) |
| | | | | $Br_2$ | ~ 0.03 | | | | | | | | | |
| .3 | $CD_3NO_2 + H_2O \rightarrow CH_2{:}NO_2^- + H_2DO^+$ | $H_2O$ | A ~ 0.15 - 0.7 | $H_2SO_4$ | ~ 0.15 | $k$ AB | 70 | 3.3 | -8 | | | | * | ([8]) |
| | | | | $Br_2$ | ~ 0.03 | | | | | | | | | |
| .4 | $CD_3NO_2 + D_2O \rightarrow CD_2{:}NO_2^- + D_3O^+$ | $D_2O$ | A ~ 0.15 - 0.7 | $H_2SO_4$ | ~ 0.15 | $k$ AB | 70 | 1.4 | -8 | | | | * | ([8]) |
| | | | | $Br_2$ | ~ 0.03 | | | | | | | | | |
| .5 | $CH_3NO_2 + OH^- \rightarrow CH_2{:}NO_2^- + H_2O$ | $H_2O$ | 0.017 - 0.027 | | | $k$ AB | 0 | 4.0 | +1 | | | | * | ([4]) |



942151 O—51——27

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $CH_3NO_2 + CH_3COO^- \rightarrow CH_2NO_2^- + CH_3COOH$ | $H_2O$ | A ~ 0.15 - 0.7 | $CH_3COOH$ | 0.1 - 0.2 | $k$ AB | 11 | 1.6 | -5 | | | | * | (8) |
| | | | B ~ 0.1 - 0.5 | $Br_2$ | ~ 0.03 | | 25 | 7.7 | -5 | | | | | |
| | | | | | | | 35 | 2.3 | -4 | 20 | | | | |
| | | $D_2O$ | " | " | " | " | 25 | 6.6 | -5 | | | | | " |
| .7 | $CD_3NO_2 + CH_3COO^- \rightarrow CD_2{:}NO_2^- + CH_3COOD$ | $H_2O$ | A ~ 0.15 - 0.7 | $CH_3COOH$ | 0.1 - 0.2 | $k$ AB | 25 | 1.2 | -5 | | | | * | (8) |
| | | | B ~ 0.1 - 0.5 | $Br_2$ | ~ 0.03 | | | | | | | | | |
| | | $D_2O$ | " | " | " | " | 11 | 1.9 | -6 | | | | * | " |
| | | | | | | | 25 | 9.6 | -6 | | | | | |
| | | | | | | | 35 | 2.4 | -5 | 20 | | | | |
| .8 | $CH_3NO_2 + CH_2OHCOO^- \rightarrow CH_2{:}NO_2^- + CH_2OHCOOH$ | $H_2O$ | A = 0.05 | $CH_2OHCOOH$ | ~ 0.1 | $k$ AB | 20 | 1.05 | +1 | | | | * | (7) |
| | | | B = 0.08 - 0.15 | $Br_2$ | 0.002 - 0.012 | | | | | | | | | |
| .9 | $CH_3NO_2 + CH_2ClCOO^- \rightarrow CH_2{:}NO_2^- + CH_2ClCOOH$ | $H_2O$ | A ~ 0.15 - 0.7 | $CH_2ClCOOH$ | 0.20 - 0.25 | $k$ AB | 11 | 8.4 | -7 | | | | * | (8) |
| | | | B = 0.2 - 0.7 | $Br_2$ | ~ 0.03 | | 25 | 4.2 | -6 | | | | | |
| | | | | | | | 35 | 1.3 | -5 | 20 | | | | |
| | | $D_2O$ | " | " | " | " | 25 | 3.1 | -6 | | | | | " |
| .10 | $CD_3NO_2 + CH_2ClCOO^- \rightarrow CD_2{:}NO_2^- + CH_2ClCOOH$ | $H_2O$ | A ~ 0.15 - 0.7 | $CH_2ClCOOH$ | 0.20 - 0.25 | $k$ AB | 25 | 9.6 | -7 | | | | * | (8) |
| | | | B = 0.2 - 0.7 | $Br_2$ | ~ 0.03 | | 35 | 3.0 | -6 | | | | | |
| | | $D_2O$ | " | " | " | " | 25 | 4.6 | -7 | | | | * | " |
| | | | | | | | 35 | 2.0 | -7 | 21 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $C_2H_5NO_2 + H_2O \rightarrow CH_3CH{:}NO_2^- + H_3O^+$ | $H_2O$ buffers | ~ 0.001 | pH | 6.1 | $k$ A | 25 | 1.16 | −4 | | | | | ([5]) ([9]) |
| | | | | | 7.0 | | " | 1.54 | −4 | | | | | |
| | | | | | 8.0 | | " | 3.00 | −4 | | | | | |
| | | | | | 8.9 | | " | 3.67 | −4 | | | | | |
| | | | | | 10.0 | | " | 1.13 | −3 | | | | | |
| | | | | | 10.9 | | " | 3.17 | −3 | | | | | |
| .12 | $C_2H_5NO_2 + OH^- \rightarrow CH_3CH{:}NO_2^- + H_2O$ | $H_2O$ | ~ 0.02 − 0.05 | | | $k$ AB | 0 | 6.52 | −1 | 12 | 3.2 | 9 | * | ([6]) ([10]) |
| | | | | | | | 5 | 9.85 | −1 | $\Delta H_a$ = 12.1; | $\Delta S_a$ = −15.5 | | | ([3]) ([4]) |
| .13 | $C_2H_5NO_2 + OD^- \rightarrow CH_3CH{:}NO_2^- + HDO$ | $D_2O$ | 0.015 − 0.027 | | | $k$ AB | 0 | 9.3 | −1 | 11.5 | 1.26 | 9 | * | ([10]) |
| | | | | | | | 5 | 1.39 | 0 | | $\Delta S_a$ = −16.4 | | | ([3]) |
| .14 | $CH_3CHDNO_2 + OD^- \rightarrow CH_3CD{:}NO_2^- + HDO$ | $D_2O$ | 0.015 − 0.027 | | | $k$ AB | 0 | (6.0) | −1 | | | | * | ([10]) |
| | | | | | | | " | 3.5 | −1 | 10.7 | 1.26 | 8 | | ([3]) |
| | | | | | | | 5 | 4.6 | −1 | | $\Delta S_a$ = 21.2 | | | ([3]) |
| .15 | $CH_3CD_2NO_2 + OD^- \rightarrow CH_3CD{:}NO_2^- + D_2O$ | $D_2O$ | A = B ~ 0.05 − 0.065 | | | $k$ AB | 0 | (~ 1.0) | −1 | | | | * | ([10]) |
| .16 | $C_2H_5NO_2 + NH_3 \rightarrow CH_3CH{:}NO_2^- + NH_4^+$ | $H_2O$ | 0.021 | | | $k$ AB | 0 | 9.5 | −4 | | | | * | ([6]) ([4]) |
| | | | 0.065 | | | | " | 7.8 | −4 | | | | | |
| | | | 0.021 | | | | 5.2 | 1.6 | −3 | $\Delta H_a$ = 14.9 | $\Delta S_a$ = −17.9 | | | ([4]) |
| | | | 0.065 | | | | " | 1.3 | −3 | | | | | |
| .17 | $C_2H_5NO_2 + CH_3NH_2 \rightarrow CH_3CH{:}NO_2^- + CH_3NH_3^+$ | $H_2O$ | 0.021 | | | $k$ AB | 0 | 1.44 | −2 | | | | * | ([6]) ([4]) |
| | | | 0.065 | | | | " | 1.30 | −2 | | | | | |
| | | | 0.021 | | | | 5.2 | 2.46 | −2 | $\Delta H_a$ = 15.0 | $\Delta S_a$ = −12.0 | | | ([4]) |
| | | | 0.065 | | | | " | 2.35 | −2 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .18 | $C_2H_5NO_2 + (CH_3)_2NH \rightarrow CH_3CH{:}NO_2^- + (CH_3)_2NH_2^+$ | $H_2O$ | 0.0173 | | | $k$ AB | 0 | 4.34 | -2 | | | | * | (6) (4) |
| | | | 0.051 | | | | " | 4.08 | -2 | | | | | |
| | | | 0.024 | | | | 5.2 | 7.58 | -2 | $\Delta H_a = 15.9$ | $\Delta S_a$ | | | |
| | | | 0.046 | | | | " | 7.36 | -2 | | -6.6 | | | (4) |
| .19 | $C_2H_5NO_2 + (CH_3)_3N \rightarrow CH_3CH{:}NO_2^- + (CH_3)_3NH^+$ | $H_2O$ | 0.033 | | | $k$ AB | 0 | 3.43 | -2 | | | | * | (6) (4) |
| | | | 0.045 | | | | " | 3.41 | -2 | | | | | |
| | | | 0.020 | | | | 5.2 | 6.13 | -2 | $\Delta H_a = 15.8$ | | | | (4) |
| | | | 0.045 | | | | " | 6.00 | -2 | | -7.3 | | | |
| .20 | $C_3H_7NO_2 + H_2O \rightarrow C_2H_5CH{:}NO_2^- + H_3O^+$ | $H_2O$ buffers | ~ 0.001 | pH | 8.0 | $k$ A | 25 | 1.57 | -4 | | | | | (5) (9) |
| | | | | | 8.9 | | " | 2.34 | -4 | | | | | |
| | | | | | 10.0 | | " | 7.34 | -4 | | | | | |
| .21 | $C_3H_7NO_2 + OH^- \rightarrow C_2H_5CH{:}NO_2^- + H_2O$ | $H_2O$ | 0.017 - 0.027 | | | $k$ AB | 0 | 4.9 | -1 | | | | | (3) (2) |
| .22 | $(CH_3)_2CHNO_2 + H_2O \rightarrow (CH_3)_2C{:}NO_2^- + H_3O^+$ | $H_2O$ buffers | ~ 0.001 | pH | 8.0 | $k$ A | 25 | 1.30 | -4 | | | | | (5) (9) |
| | | | | | 8.9 | | | 1.35 | -4 | | | | | |
| | | | | | 10.0 | | | 1.50 | -4 | | | | | |
| | | | | | 10.9 | | | 3.17 | -4 | | | | | |
| .23 | $(CH_3)_2CHNO_2 + OH^- \rightarrow (CH_3)_2C{:}NO_2^- + H_2O$ | $H_2O$ | 0.017 - 0.027 | | | $k$ AB | 0 | 3.5 | -2 | | | | | (3) |
| | | | | | | | 5 | 5.6 | -2 | | | | | |

## COMMENTS

**General.** Reverse reactions of proton elimination from C – N bond, see 622.450.

**Methods.** ([5]) Reactions (.1) (.11) (.20) (.22) (.23) polarography of A. ([1])([7])([8]) Reactions (.1) (.2) (.3) (.4) (.6) (.7) (.8) (.9) (.10), derived from substitution reactions of the type $CH_3NO_2 + 3Br_2 \rightarrow CBr_3NO_2 + 3HBr$ (see 312.471) in the presence of the stated acid. ([3])([4])([6])([10]) Reactions (.5) (.12) (.13) (.14) (.15) (.16) (.17) (.18) (.19) (.21) (.23), electric conductivity measurements.

**Reactions.** (.10) $k$ at 25° (in $H_2O$) extrapolated. (.12) $k$ data of ([6]) and ([10]) in agreement; $k$ varies slightly in the course of the reaction ([10]). Reverse reaction negligible except at later stages ([6]). (.14) Discrepancy between $k$ of ([10]) and ([3]) at 0°C; value of ([3]) more reliable, ([10]) claiming no precision. Accompanying reaction $CH_3CDHNO_2 + OD^- \rightarrow CH_3CHNO_2 + D_2O$ has apparently no effect on $k$. (.15) No precision claimed; $k$ decreases with time and on repeated experiments, because of the presence of some incompletely deuterated substrate. (.16) (.17) (.18) (.19) Reverse reaction negligible except at late stages.

## LITERATURE

([1]) R. Junell, *ZPC*[A] 1929, **141**, 71. ([2]) R. Junell, *Svensk. Kin. Tid.*, 1934, **46**, 125. ([3]) S. H. Maron, V. K. LaMer, *ACS* 1938, **60**, 2588. ([4]) S. H. Maron, V. K. LaMer, *ACS* 1938, **60**, 2591. ([5]) E. W. Miller, A. P. Arnold, M. J. Astle, *ACS* 1948, **70**, 3971. ([6]) R. G. Pearson, *ACS* 1948, **70**, 204. ([7]) K. J. Pedersen, *Dansk. Videnskap. Selskap. Mat.-fysiske Medd.* 1932, **12**, 1. ([8]) O. Reitz, *ZPC*[A] 1936, **176**, 363. ([9]) D. Turnbull, S. H. Maron, *ACS* 1943, **65**, 212. ([10]) W. F. K. Wynne-Jones, *JCP* 1934, **2**, 381.

# ELIMINATION
## of Hydrogen halide
## Double Bond Formation



Reaction type

$$R_1CHXCH_2R_2 + ROH \rightarrow R_1CH{:}CHR_2 + X^- + ROH_2^+$$
(A) (B) (L) (M) (N)

$$R_1CHXCH_2R_2 + OR^- \rightarrow R_1CH{:}CHR_2 + X^- + ROH$$

Rate measured + dM/d*t*

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, see at the end of the table.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_5Br + OC_2H_5^-$ | $C_2H_5OH$ | B = 0.05 | | | *k*AB | 54.9 | 1.97 | -4 | | | | | (5) |
| | | | 0.1 | | | | | 1.74 | -4 | | | | | |
| | | | 2.0 | | | | | 1.19 | -4 | | | | | |
| .2 | $COOHCHClCHClCOOH + H_2O$ | $H_2O$ | | | | *k*A | 70 | 5.06 | -6 | | | | | (14) |
| | | | | | | | 80 | 1.11 | -5 | | | | | |
| | | | | | | | 89 | 2.50 | -5 | | | | | |
| .3 | $COOHCHClCHClCOOH + OH^-$ | $H_2O$ | A = 0.15 | | | *k*AB | 25 | 3.17 | -6 | | | | | (14) |
| .4 | *iso*-$COOHCHClCHClCOOH + H_2O$ | $H_2O$ | A = 0.03 | | | *k*A | 60 | 3.33 | -6 | | | | | (14) |
| | | | | | | | 70 | 9.08 | -6 | | | | | |
| | | | | | | | 80 | 2.23 | -5 | | | | | |
| | | | | | | | 90 | 6.19 | -5 | | | | | |
| .5 | *iso*-$COOHCHClCHClCOOH + OH^-$ | $H_2O$ | A = B = 0.086 | | | *k*AB | 25 | 1.49 | -5 | | | | * | (14) |
| | | | | | | | → | 8.1 | -6 | | | | | |
| .6 | $CH_2ClCH_2SO_3Na + OH^-$ | $H_2O$ | | | | *k*AB | 1.1 | 2.42 | -4 | | | | | (13) |
| | | | | | | | 9.5 | 4.44 | -4 | | | | | |
| | | | | | | | 25 | 1.79 | -3 | 17.4 | 1.3 | 9 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .7 | $(CH_3)_2CHCl + OH^-$ | Et80 | | | | $k$AB | 70 | 6.78 | -6 | | | | * | (10) |
| | | | | | | | 80 | 1.89 | -5 | | | | | |
| | | | | | | | 90 | 5.06 | -5 | 24.8 | 4.8 | 10 | | |
| .8 | $(CH_3)_2CHBr + C_2H_5OH$ | $C_2H_5OH$ | | $H_2SO_4$ | | $k$A | 54.9 | 1.73 | -7 | | | | | (5) |
| .9 | $(CH_3)_2CHBr + OC_2H_5^-$ | $C_2H_5OH$ | B = 0.05 | | | $k$AB | 54.9 | 2.01 | -5 | | | | | (5) |
| | | | 0.1 | | | | " | 2.12 | -5 | | | | | |
| | | | 2.0 | | | | " | 9.7 | -6 | | | | | |
| .10 | $(CH_3)_2CHBr + OH^-$ | Et60 | A = 0.1; B = 0.85 | | | $k$AB | 45 | 1.57 | -5 | | | | * | (7) |
| | | | | | | | 60 | 7.52 | -5 | | | | | |
| | | | | | | | 75 | 3.20 | -4 | 22.0 | 2.8 | 10 | | |
| | | Et80 | " | " | | $k$AB | 50 | 3.89 | -5 | | | | * | (7) (10) |
| | | | | | | | 80 | 7.78 | -4 | 22.6 | 8.3 | 10 | | |
| .11 | $(CH_3)_2CHI + OH^-$ | Et60 | | | | $k$AB | 50 | 1.22 | -4 | | | | * | (10) |
| | | | | | | | 69.8 | 9.08 | -4 | | | | | |
| | | | | | | | 80.0 | 2.31 | -3 | 22.2 | 1.4 | 11 | | |
| .12 | $(CH_3)_3CCl + H_2O$ (See Supplementary table) | Et80 | A = 0.09 | NaOH | 0-0.1 | $k$A | 25 | 1.44 | -6 | | | | * | (3) |
| .13 | $(CH_3)_3CBr + C_2H_5OH$ | $C_2H_5OH$ | | $H_2SO_4$ | | $k$A | 54.9 | 1.98 | -4 | | | | | (5) |
| .14 | $(CH_3)_3CBr + OC_2H_5^-$ | $C_2H_5OH$ | B = 0.02 | | $k_1$A + $k_2$AB | | 54.9 | | | | | | * | (5) |
| | | | 0.05 | | | | $k_1$ | 2.33 | -4 | | | | | |
| | | | 2.0 | | | | $k_1$ | 2.42 | -4 | | | | | |
| | | | | | | | $k_2$ | 5.0 | -5 | | | | | |
| .15 | $(CH_3)_3CBr + H_2O$ (See Supplementary table) | Et80 | A = 0.173 | | | $k$A | 25 | 4.69 | -5 | | | | * | (3) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .16 | $(CH_3)_3CI + H_2O$ | Et80 | A = 0.173 | | | $k$ A | 25 | 1.16 | -4 | | | | * | (3) |
| | (See Supplementary table) | | | | | | | | | | | | | |
| .17 | $(C_2H_5)(CH_3)_2CCl + H_2O$ | Et60 | A = 0.078 | | | $k$ A | 25.2 | 1.10 | -4 | | | | * | (9) |
| | (See Supplementary table) | Et80 | A = 0.078 | | | $k$ A | 25.2 | 1.00 | -5 | | | | * | (9) |
| | | | 0.16 | | | | " | 9.41 | -6 | | | | | |
| | | | 0.147 | | | | 50.0 | 1.15 | -4 | | | | | |
| | | Et80 | A = 0.078 | NaOH | 0.2 | $k$ A | 25.2 | 1.01 | -5 | | | | * | (9) |
| .18 | $(C_2H_5)(CH_3)_2CBr + H_2O$ | Et80 | A = 0.07 | | | $k$ A | 25.2 | 4.30 | -4 | | | | * | (9) |
| | (See Supplementary table) | " | A = 0.06 | NaOH | 0.12 | $k$ A | 25.2 | 4.01 | -4 | | | | * | (9) |
| .19 | $(C_2H_5)(CH_3)_2CI + H_2O$ | Et80 | A = 0.13 | | | $k$ A | 25.2 | 1.29 | -3 | | | | * | (9) |
| | (See Supplementary table) | " | A = 0.12 | NaOH | 0.12 | $k$ A | 25.2 | 1.34 | -3 | | | | * | (9) |
| .20 | $C_6H_{13}CH(CH_3)Cl + H_2O$ | Et60 | | | | $k$ A | 100 | 1.05 | -6 | | | | * | (8) |
| | (See Supplementary table) | | | | | | | | | | | | | |
| .21 | $C_6H_{13}CH(CH_3)Br + H_2O$ | Et60 | | | | $k$ A | 100 | 3.75 | -5 | | | | * | (8) |
| | (See Supplementary table) | | | | | | | | | | | | | |
| .22 | $C_6H_{13}CH(CH_3)Br + OH^-$ | Et60 | A = 0.057; | B = 0.80 | | $k$ AB | 80.0 | 4.40 | | | | | | (11) |
| | **Aryl-substituted aliphatic halide** | | | | | | | | | | | | | |
| .23 | $C_6H_5CH_2CH_2Br + C_2H_5OH$ | $C_2H_5OH$ | | | | $k$ A | 54.9 | 1.92 | -4 | | | | * | (5) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .24 | $C_6H_5CH_2CH_2Br + OC_2H_5^-$ | $C_2H_5OH$ | B = 1.5 | | | $k$ AB | 54.9 | 1.5 | -4 | | | | * | (5) |
| | | | 2.5 | | | | " | 1.6 | -4 | | | | | |
| .25 | $C_6H_5CH(CH_3)Br + OC_2H_5^-$ | $C_2H_5OH$ | B = 0.05 | | | $k$ AB | 54.9 | 6.58 | -4 | | | | | (5) |
| | | | 0.1 | | | | " | 5.93 | -4 | | | | | |
| .26 | $(C_6H_5)_2CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 3.7 | -4 | | | | | (1) |
| | | | | | | | 30.4 | 1.27 | -3 | 21.3 | | | | |
| .27 | $(p\text{-}CH_3C_6H_4)_2CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 1.1 | -4 | | | | | (1) |
| | | | | | | | 30.4 | 3.7 | -4 | 21.0 | | | | |
| .28 | $(p\text{-}CH_3OC_6H_4)_2CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 9.2 | -4 | | | | | (1) |
| | | | | | | | 30.4 | 3.0 | -3 | 20.6 | | | | |
| .29 | $[p\text{-}(CH_3)_3CC_6H_4]_2CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 1.1 | -4 | | | | | (1) |
| | | | | | | | 30.4 | 3.4 | -4 | 19.8 | | | | |
| .30 | $[p\text{-}NO_2C_6H_4CH_2CH_2N(CH_3)_3]Br$ | $H_2O$ | 0.3 | | | $k$ A | 100 | 4.0 | -5 | | | | | (4) |
| | $\rightarrow NO_2C_6H_4CH{:}CH_2 + N(CH_3)_3.HBr$ | | | | | | | | | | | | | |
| .31 | $[p\text{-}NO_2C_6H_4CH_2CH_2N(CH_3)_3]I$ | $H_2O$ | 0.3 - 0.6 | | | $k$ A | 100 | 4.0 | -5 | | | | | (4) |
| | $\rightarrow NO_2C_6H_4CH{:}CH_2 + N(CH_3)_3.HI$ | | | | | | | | | | | | | |
| .32 | $(p\text{-}FC_6H_4)_2CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 3.03 | -3 | | | | | |
| | | | | | | | 30.4 | 9.4 | -3 | 19.5 | | | | (1) |
| .33 | $(p\text{-}ClC_6H_4)_2CHCH_2Cl + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 9.1 | -4 | | | | | (1) |
| | | | | | | | 30.4 | 2.82 | -3 | 19.5 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .34 | $(p\text{-}ClC_6H_4)_2CHCHCl_2 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 5.67 | -3 | | | | | (1) |
| | | | | | | | 30.4 | 1.72 | -2 | 19.1 | | | | |
| .35 | $(p\text{-}ClC_6H_4)_2CHCCl_3 + OH^-$ | $H_2O + C_2H_5OH$ | 76.0 wt% | | | $k$ AB | 20.1 | 1.32 | -2 | | | | | (1) |
| | | | 87.0 | | | | " | 1.89 | -2 | | | | | |
| | | | 92.6 | | | | " | 2.48 | -2 | | | | | |
| | | | " | | | | 30.4 | 7.11 | -2 | 18.2 | | | | |
| .36 | $(p\text{-}ClC_6H_4)(C_6H_5)CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 3.01 | -3 | | | | | |
| | | | | | | | 30.4 | 1.0 | -2 | 19.0 | | | | (1) |
| .37 | $(p\text{-}BrC_6H_4)_2CHCCl_3 + OH^-$ | Et92.6wt | | | | $k$ AB | 20.1 | 3.47 | -2 | | | | | (1) |
| | | | | | | | 30.4 | 1.03 | -1 | 18.8 | | | | |
| | **Aromatization** | | | | | | | | | | | | | |
| .38 | $\alpha\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$ | | See Supplementary table | | | | | | | | | | | |
| .39 | $\alpha\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$ | Et76 | A ~ 0.001; B ~ 0.005 | | | $k$ AB | 20.1 | 1.7 | -1 | | | | * | (2) |
| .40 | $\alpha\text{-}C_6H_6Cl_3 + 3\ C_5H_{10}NH \rightarrow C_6H_3Cl_3 + 3\ C_5H_{10}NH.HCl$ | Et95 | A = 0.0125; B = 0.0375 | | | $k$ AB | 56.2 | 2.0 | -3 | | | | * | (15) |
| | | | | | | | 79.5 | 1.25 | -2 | 19.5 | 2 | 10 | | |
| .41 | $\beta\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$ | Et76 | See (.42) | | | | | | | | | | | (2) |
| .42 | $\beta\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$ | Et76 | A ~ 0.001; B ~ 0.005 | | | $k$ AB | 20.1 | ~ 3 | -6 | | | | | (2) |
| .43 | $\gamma\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$ | | See Supplementary table | | | | | | | | | | | |
| .44 | $\gamma\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$ | Et76 | A ~ 0.001; B ~ 0.005 | | | $k$ AB | 20.1 | 4.4 | -2 | | | | * | (2) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .45 | $\gamma$-$C_6H_6Cl_6 + 3\ C_5H_{10}NH \rightarrow C_6H_3Cl_3 + 3\ C_5H_{10}NH.HCl$ | Et95 | A = 0.0125; B = 0.0375 | | | $k$ AB | 56.2 | 9.2 | -4 | | | | * | (15) |
| | | | | | | | 79.5 | 3.4 | -3 | 13.8 | 1 | 6 | | |
| .46 | $\delta$-$C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$ | See Supplementary table | | | | | | | | | | | | |
| .47 | $\delta$-$C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$ | Et76 | | | | | 20.1 | fast | | | | | * | (2) |
| .48 | $C_6H_5Cl_5 + OH^- \rightarrow C_6H_4Cl_4 + Cl^- + H_2O$ | Et76 | A ~ 0.001; B ~ 0.005 | | | $k$ AB | 20.1 | 1.1 | -1 | | | | * | (2) |
| .49 | $C_6H_4Cl_4 + OH^- \rightarrow C_6H_3Cl_3 + Cl^- + H_2O$ | Et76 | A ~ 0.001; B ~ 0.005 | | | | 20.1 | fast | | | | | * | (2) |
| .50 | $\delta$-$C_6H_6Cl_6 + 3\ C_5H_{10}NH \rightarrow C_6H_3Cl_3 + 3\ C_5H_{10}NH.HCl$ | Et95 | A = 0.0125; B = 0.0375 | | | $k$ AB | 56.2 | 1.3 | -3 | | | | * | (15) |
| | | | | | | | 79.5 | 1.19 | -2 | 20.4 | 6 | 10 | | |
| .51 | $\epsilon$-$C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$ | See Supplementary table | | | | | | | | | | | | |

## SUPPLEMENTARY TABLES

**Simultaneous first-order hydrolysis and elimination.**

Reactions **(.12) (.15) (.16) (.17) (.18) (.19) (.20) (.21)**

$k_E$ = first-order $k$ for the elimination reaction

$k_S$ = first-order $k$ for the hydrolysis

$k_t = k_E + k_S$ = first-order $k$ for the total reaction (elimination + substitution)

$k_t$ is the rate of formation of the carbonium ion, assumed to be the rate determining step.

| Reaction | Temperature | $10^5 k_E$ | $10^5 k_S$ | $10^5 k_t$ | $k_E/k_t$ |
|---|---|---|---|---|---|
| (.12) $(CH_3)_3CCl + H_2O$ | 25 | 0.144 | 0.710 | 0.854 | 0.168 |
| (.15) $(CH_3)_3CBr + H_2O$ | 25 | 4.69 | 32.5 | 37.2 | 0.126 |
| (.16) $(CH_3)_3CI + H_2O$ | 25 | 11.6 | 78.5 | 90.1 | 0.129 |
| (.17) $(C_2H_5)(CH_3)_2CCl + H_2O$ | 25 | 1.00 | 0.500 | 1.50 | 0.333 |
| (.18) $(C_2H_5)(CH_3)_2CBr + H_2O$ | 25 | 43.0 | 15.3 | 58.3 | 0.262 |
| (.19) $(C_2H_5)(CH_3)_2CI + H_2O$ | 25 | 128.8 | 45.2 | 174 | 0.260 |
| (.20) $C_6H_{13}C(CH_3)Cl + H_2O$ | 100 | 0.105 | 0.700 | 0.805 | 0.13 |
| (.21) $C_6H_{13}C(CH_3)Br + H_2O$ | 100 | 3.75 | 23.0 | 26.8 | 0.14 |

## SUPPLEMENTARY TABLES *(continued)*

**Aromatization**

*Solvent* $CH_3OH$ . A ~ 5g/l; B = 0.1 *M* . *Temperature* 0° C (12)

| Reaction | Fraction of reaction completed | Time (Hours) |
|---|---|---|
| (.36) $\alpha - C_6H_6Cl_6 + 3\ OH^-$ | 0.27 | 0.5 |
| | 0.049 | 1.0 |
| (.40) $\gamma - C_6H_6Cl_6 + 3\ OH^-$ | 0.30 | 2.5 |
| | 0.56 | 5.5 |
| (.43) $\delta - C_6H_6CL_6 + 3\ OH^-$ | 0.26 | 0.75 |
| | 0.56 | 2.5 |
| (.48) $\epsilon - C_6H_6Cl_6 + 3\ OH^-$ | 0.28 | 3.0 |
| | 0.50 | 6.5 |

## SOLVENTS

Et $x$ = $H_2O + C_2H_5OH$ $x$ % (by volume, except where noted wt).

## COMMENTS

(.5) $k$ falling in the course of the reaction, possibly as a result of conversion of the *iso* form into the normal form. (.7) (.10) - (.22) Concomitant solvolysis reaction, see 212.471. (.14) First order prevailing at low alkali concentrations; $k_1$ not corrected for the few % of simultaneously present second-order reaction. (.17) (.18) (.19) Addition of NaOH in the stated amounts is practically without effect on the rate of the first-order elimination reaction, as it is on the rate of the first-order hydrolysis, and of the total reaction. (.23) (.24) With $OC_2H_5^-$ 0.05 - 0.1, about 25 - 50 % of the reaction is second-order. (.39) - (50) Configuration of product not specified. (.39) from (.38). (.42) from (.41). (.44) from (.43). (.48) from (.46); this is the rate determining step of (.46), the remaining steps (.47) and (.49) being fast.

## LITERATURE

(1) S.J.Cristol, *ACS* 1945, **67**, 1494. (2) S.J.Cristol, *ACS* 1947, **69**, 338. (3) K.A.Cooper, E.D.Hughes, C.K.Ingold, *CSL* 1937, 1280. (4) E.D.Hughes, C.K.Ingold, *CSL* **1933**, 523. (5) E.D.Hughes, C.K.Ingold, S.Masterman, B. J. McNulty, *CSL* **1940**, 899. (6) E. D. Hughes, C. K. Ingold, A. D. Scott, *CSL* **1937**, 1271. (7) E.D.Hughes, C.K.Ingold, U.G.Shapiro, *CSL* **1936**, 225. (8) E.D.Hughes, C.K.Ingold, U.G.Shapiro, *CSL* **1937**, 1277. (9) E.D.Hughes, B.J.McNulty, *CSL* **1937**, 1283. (10) E.D.Hughes, U.G.Shapiro, *CSL* **1937**, 1177. (11) E.D.Hughes, U.G.Shapiro, *CSL* **1937**, 1192. (12) K.C.Kauer, R.B.Duvall, F.N.Alquist, *IEC* 1947, **39**, 1335. (13) E.F.Landau, W.F.Whitmore, P.Doty, *ACS* 1946, **68**, 816. (14) H.Y.W.Robinson, D.T.Lewis, *CSL* **1933**, 1260. (15) D.J.Whittingham, D.L.Garmaise, *CJR*[B] 1949, **27**, 415.

# ELIMINATION

## Bond Unsaturation

*Liquid phase*

### Elimination of hydrogen halide from C, N bond (Chlorimine → Nitrile)

Reaction type $ArCH{:}NX + OR^- \rightarrow ArCN + HOR + X^-$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | $\Delta S_a$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 1.67 | -2 | | | | | (1) (2) |
| | | | | 30 | 6.2 | -1 | 19.8 | 1.2 | 14 | +1.3 | |
| .2 | o - $CH_3C_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 4.45 | -2 | | | | | (1) |
| .3 | p - $CH_3C_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 8.66 | -3 | | | | | (1) |
| .4 | o - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 2.84 | -3 | | | | | (1) |
| .5 | m - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 1.83 | -2 | | | | | (1) |
| | | $H_2O$ + dioxane 50 % | $k$ AB | 0 | 4.83 | -3 | | | | | (1) |
| .6 | p - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O$ + dioxane 50 % | $k$ AB | 0 | 5.0 | -3 | | | | | (1) |
| | | $H_2O + C_2H_5OH$ 80 % | $k$ AB | 0 | 4.00 | -3 | | | | | (1) |
| | | 92.5 % | $k$ AB | 0 | 4.7 | -3 | | | | | (1) |
| | | 95 % | $k$ AB | 0 | 4.7 | -3 | | | | | (2) |
| | | | | 30 | 1.8 | -1 | 19.9 | 1.0 | 14 | -0.6 | |



942151 O—51——28

| No. | Reaction | Solvent | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | $\Delta S_a$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $p$ - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$ *(continued)* | $C_2H_5OH$ (100%) | $k$ AB | 0 | 4.9 | -3 | | | | | (2) |
| | | | | 30 | 1.5 | -1 | 17.0 | 6.1 | 11 | -6.9 | |
| .7 | $p$ - $CH_3OC_6H_4CH{:}NCl + OCH_3^-$ | $H_2O + CH_3OH$ 95 % | $k$ AB | 0 | 5.6 | -4 | | | | | (2) |
| | | | | 30 | 2.7 | -2 | 21.3 | 4.7 | 14 | 0 | |
| | | $CH_3OH$ (100%) | $k$ AB | 0 | 3.5 | -4 | | | | | (2) |
| | | | | 10 | 2.07 | -3 | | | | | |
| | | | | 30 | 2.27 | -2 | 20.6 | 4.3 | 14 | -2.4 | |
| .8 | 3, 4 - $CH_2O_2C_6H_3CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 6.72 | -3 | | | | | (1) (2) |
| | | | | 30 | 2.77 | -1 | 20.4 | 1.5 | 14 | -1.6 | |
| .9 | $C_6H_5CH{:}CHCH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 5.8 | -3 | | | | | (1) (3) |
| | | | | 30.5 | 2.3 | -1 | 20.1 | 1.8 | 14 | -0.3 | |
| .10 | $o$ - $C_4H_3OCH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 6.32 | -1 | | | | | (1) |
| .11 | $o$ - $NO_2C_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 9.0 | 0 | | | | | (1) |
| .12 | $m$ - $NO_2C_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 5.27 | -1 | | | | | (1) |
| .13 | $p$ - $NO_2C_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 1.30 | 0 | | | | | (1) |
| .14 | 3 - $NO_2$-4-$CH_3O$-$C_6H_3CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 9.65 | -2 | | | | | (1) |
| .15 | $o$ - $ClC_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 1.28 | -1 | | | | | (1) |
| | | $H_2O$ + dioxane 50 % | $k$ AB | 0 | 6.16 | -2 | | | | | (1) |
| .16 | $m$ - $ClC_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O + C_2H_5OH$ 92.5 % | $k$ AB | 0 | 1.02 | -1 | | | | | (1) |
| .17 | $p$ - $ClC_6H_4CH{:}NCl + OC_2H_5^-$ | $H_2O$ + dioxane 50 % | $k$ AB | 0 | 2.83 | -2 | | | | | (1) |

| No. | Reaction | Solvent | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | $\Delta S_a$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .17 | $p$ - $ClC_6H_4CH{:}NCl + OC_2H_5^-$ *(continued)* | $H_2O + C_2H_5OH$ 80 % | $k$ AB | 0 | 3.93 | −2 | | | | | (1) |
| | | 92.5 | $k$ AB | 0 | 4.67 | −2 | | | | | (1) |
| | | 95 | $k$ AB | 0 | 5.0 | −2 | | | | | (2) |
| | | | | 30 | 1.8 | 0 | 20.1 | 1.4 | 15 | +4.6 | |
| | | $C_2H_5OH$ (100%) | $k$ AB | 0 | 6.0 | −2 | | | | | (2) |
| | | | | 30 | 1.4 | 0 | 17.4 | 1 | 13 | −4.8 | |
| .18 | $p$ - $ClC_6H_4CH{:}NCl + OCH_3^-$ | $H_2O + CH_3OH$ 95 % | $k$ AB | 0 | 5.1 | −3 | | | | | (2) |
| | | | | 10 | 1.82 | −2 | | | | | |
| | | | | 30 | 1.77 | −1 | 20.1 | 1.7 | 14 | 0 | |
| | | $CH_3OH$ (100%) | $k$ AB | 0 | 4.5 | −3 | | | | | (2) |
| | | | | 10 | 1.61 | −2 | | | | | |
| | | | | 30 | 1.59 | −1 | 19.5 | 4.7 | 13 | −2.3 | |
| .19 | $p$ - $ClC_6H_4CH{:}NCl + (C_2H_5)_3N \rightarrow$ $p$ - $ClC_6H_4CN + (C_2H_5)_3N.HCl$ | $CH_3OH$ (100%) | $k$ AB | 25 | 4.0 | −5 | | | | | (2) |
| | | | | 40 | 1.7 | −4 | 17.6 | 3.5 | 8 | −22.1 | |
| | | $C_6H_6$ | $k$ AB | 30 | 2.5 | −5 | | | | | (2) |
| | | | | 40 | 4.4 | −5 | 11.9 | 1.5 | 4 | −44.5 | |

## LITERATURE

(1) C. R. Hauser, J. W. Lemaitre, A. E. Rainford, *ACS* 1935, **57**, 1056.

(2) W. E. Jordan, H. E. Dyas, D. G. Hill, *ACS* 1941, **63**, 2383.

# ELIMINATION
## of halogen molecule by halogen ions, with charge exchange



Reaction type $RCHXCHXR' + 2\ X'^{-} \rightarrow RCH{:}CHR' + X'_2 + 2\ X^{-}$

(A) (B) (L) (M)

or $RCHXCHXR' + 3\ X'^{-} \rightarrow RCH{:}CHR' + X'^{-}_3 + 2\ X^{-}$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^{o} \times 10^{n}$ $k^{o}$ | $n$ | $E$ | $\Delta H_a$ | $\Delta S_a$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_2BrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B = 0.25 | $k$ AB | 59.7 | 8.30 | -5 | | | | (2) |
| | | | | | 74.9 | 3.70 | -4 | 23.2 | 0 | 0 | |
| .2 | $CH_3CHBrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B = 0.25 | $k$ AB | 59.7 | 3.13 | -6 | | | | (2) |
| | | | | | 74.9 | 1.61 | -5 | 25.2 | 2.0 | -0.5 | |
| .3 | $CH_2OHCHBrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B = 0.25 | $k$ AB | 59.6 | 5.35 | -6 | | | | (2) |
| | | | | | 74.9 | 2.70 | -5 | 25.2 | 2.0 | 0.4 | |
| .4 | $COOHCHBrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B = 0.25 | $k$ AB | 44.7 | 2.85 | -5 | | | | (2) |
| | | | | | 59.4 | 1.15 | -4 | | | | |
| | | | | | 79.4 | 4.62 | -4 | | | | |
| | | | | | 85.4 | 1.10 | -3 | 20.9 | 2.3 | 6.3 | |
| .5 | $C_2H_5CHBrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B = 0.25 | $k$ AB | 59.7 | 4.12 | -6 | | | | (2) (1) |
| | | | | | 74.9 | 2.20 | -5 | 25.8 | 2.6 | 1.8 | |
| .6 | *meso*-$CH_3CHBrCHBrCH_3 + 2\ I^- \rightarrow$ *trans* | $CH_3OH$ 99 % | A = 0.033; B = 0.22 | $k$ AB | 59.7 | 2.50 | -6 | | | | (3) (1) |
| | | | | | 74.9 | 1.55 | -5 | 28.0 | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $\Delta H_a$ | $\Delta S_a$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .7 | *rac*-$CH_3CHBrCHBrCH_3$ + 2 I → *cis* | $CH_3OH$ 99 % | A = 0.025; B = 0.25 | *k* AB | 59.7 | 1.28 | -6 | | | | (3) (1) |
| | | | | | 74.9 | 8.36 | -6 | 28.6 | | | |
| .8 | *meso*-COOHCHBrCHBrCOOH + 2 $I^-$ → *trans* | $CH_3OH$ 99 % | A = 0.02; B = 0.24 | *k* AB | 59.5 | 3.27 | -4 | | | | (3) |
| | | | | | 74.5 | 1.28 | -3 | | | | |
| .9 | *rac*-COOHCHBrCHBrCOOH + 2 $I^-$ → *cis* | $CH_3OH$ 99 % | A = 0.02; B = 0.25 | *k* AB | 59.5 | 6.28 | -5 | | | | (3) |
| | | | | | 75.0 | 3.13 | -4 | 24.6 | | | |
| .10 | $C_3H_7CHBrCH_2Br$ + 2 $I^-$ | $CH_3OH$ 99 % | B = 0.25 | *k* AB | 59.6 | 5.12 | -6 | | | | (2) |
| | | | | | 74.6 | 2.48 | -5 | 24.8 | 1.6 | -0.8 | |
| .11 | *meso*-$C_2H_5CHBrCHBrCH_3$ + 2 $I^-$ → *trans* | $CH_3OH$ 99 % | A = 0.02; B = 0.25 | *k* AB | 59.5 | 4.95 | -6 | | | | (3) |
| | | | | | 75.0 | 2.64 | -5 | 25.7 | | | |
| .12 | *rac*-$C_2H_5CHBrCHBrCH_3$ + 2 $I^-$ → *cis* | $CH_3OH$ 99 % | A = 0.02; B ~ 0.2 | *k* AB | 59.5 | 2.82 | -6 | | | | (3) |
| | | | | | 75.0 | 1.58 | -5 | 26.5 | | | |
| .13 | *meso*-$C_3H_7CHBrCHBrCH_3$ + 2 $I^-$ → *trans* | $CH_3OH$ 99 % | A = 0.02; B = 0.25 | *k* AB | 59.4 | 8.10 | -6 | | | | (3) |
| | | | | | 75.0 | 3.98 | -5 | 24.5 | | | |
| .14 | *rac*-$C_3H_7CHBrCHBrCH_3$ + 2 $I^-$ → *cis* | $CH_3OH$ 99 % | A = 0.02; B = 0.26 | *k* AB | 59.4 | 2.60 | -6 | | | | (3) |
| | | | | | 75.0 | 1.39 | -5 | 25.8 | | | |
| .15 | *meso*-$C_3H_7CHBrCHBrC_3H_7$ + 2 $I^-$ → *trans* | $CH_3OH$ 99 % | A = 0.017; B = 0.25 | *k* AB | 59.6 | 7.68 | -6 | | | | (3) |
| | | | | | 75.0 | 3.78 | -5 | 25.0 | | | |
| .16 | *rac*-$C_3H_7CHBrCHBrC_3H_7$ + 2 $I^-$ → *cis* | $CH_3OH$ 99 % | A = 0.018; B = 0.24 | *k* AB | 59.5 | 5.70 | -6 | | | | (3) |
| | | | | | 75.0 | 2.99 | -5 | 25.5 | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $\Delta H_a$ | $\Delta S_a$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .17 | $C_6H_5CHBrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B ~ 0.25 | $k$ AB | 44.7 | 2.04 | -5 | | | | (2) |
| | | | | | 59.5 | 1.08 | -4 | | | | |
| | | | | | 74.5 | 4.48 | -4 | | | | |
| | | | | | 80.1 | 7.36 | -4 | | | | |
| | | | | | 85.4 | 1.12 | -3 | 21.7 | -1.5 | -4 | |
| .18 | $C_6H_5CH_2CHBrCH_2Br + 2\ I^-$ | $CH_3OH$ 99 % | B ~ 0.25 | $k$ AB | 59.6 | 5.06 | -6 | | | | (2) |
| | | | | | 74.9 | 2.54 | -5 | 24.6 | 1.4 | -1.5 | |

## LITERATURE

(1) R. F. Dillon, W. G. Young, H. J. Lucas, *ACS* 1930, **52**, 1953. (2) D. Pressman, W. G. Young, *ACS* 1944, **66**, 705. (3) W. G. Young, D. Pressman, C. D. Coryell, *ACS* 1939, **61**, 1640.

**Stereochemical relations,** See: S. Winstein, H. J. Lucas, *ACS* 1939, **61**, 1576, 1581.

# ELIMINATION

## of Hydrogen halide from Halohydrins with Ring closure



Amounts are in M/l. Rates are in M/l per sec.

Coded solvents, see at the end of the table

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_2OHCH_2F + OH^- \rightarrow CH_2 - CH_2 + F^- + H_2O$ (O) | $H_2O$ | B > A | | | $kA$ | 30 | 2.5 | -5 | | | | (2)(3) |
| | | | | | | | 40 | 8.5 | -5 | | | | |
| | | | | | | | 60 | 6.2 | -4 | 21.5 | 8.5 | 10 | |
| | | D1 55.0 | " | | | $kA$ | 60 | 7.0 | -4 | | | | " |
| | | Me 55.0 | " | | | $kA$ | 60 | 3.8 | -4 | | | | " |
| .2 | $CH_2OHCH_2Cl + OH^-$ | $H_2O$ | B > A | | | $kA$ | 0 | 2.8 | -4 | | | | (2)(3) |
| | | | | | | | 15 | 2.54 | -3 | | | | |
| | | | | | | | 25 | 1.0 | -2 | | | | |
| | | | | | | | 35 | 3.6 | -2 | 23.3 | 1.1 | 15 | |
| | | $H_2O$ | A = B = 0.091 | | | $kAB$ | 0 | 2.78 | -4 | | | | (4) |
| | | | 0.073 - 0.098 | | | | 15 | 2.57 | -3 | | | | |
| | | | 0.040 | | | | 25 | 1.01 | -2 | | | | |
| | | | 0.042 | | | | 35 | 3.6 | -2 | 23.0 | | | |
| | | " | 0.04 - 0.07 | $NaNO_3$ | 0.0915 | $kAB$ | 25 | 1.0 | -2 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_2OHCH_2Cl + OH^-$ *(continued)* | D1 64.2 | B > A | | | $kA$ | 0 | 9.0 | -5 | | | | (2)(3) |
| | | D1 75 | A = B = 0.071 | | | $kAB$ | 0 | 4.52 | -4 | | | | (4) |
| | | | 0.09 | | | | 15 | 3.33 | -3 | | | | |
| | | | 0.043 - 0.07 | | | | 25 | 1.17 | -2 | 20.9 | | | |
| | | Me 66.3 | B > A | | | $kA$ | 0 | 7.2 | -6 | | | | (2)(3) |
| | | Et 74 | A = B = 0.075 | | | $kAB$ | 0 | 5.13 | -4 | | | | (4) |
| | | | 0.067 | | | | 15 | 3.60 | -3 | | | | |
| | | | 0.040 - 0.068 | | | | 25 | 1.18 | -2 | 20.3 | | | |
| | | | 0.040 | $NaNO_3$ | 0.040 | | 25 | 1.19 | -2 | | | | |
| .3 | $CH_2OHCH_2Br + OH^- \rightarrow CH_2 - CH_2 + Br^- + H_2O$ (O) | $H_2O$ | B > A | | | $kA$ | 0 | 1.64 | -3 | | | | (2)(3) |
| | | | | | | | 5 | 3.38 | -2 | | | | |
| | | | | | | | 10 | 6.59 | -2 | 21.9 | 5.3 | 15 | |
| | | D1 64.2 | B > A | | | $kA$ | 0 | 7.6 | -2 | | | | " |
| | | Me 66.3 | B > A | | | $kA$ | 0 | 7.4 | -3 | | | | " |
| .4 | $CH_2OHCH_2I + OH^- \rightarrow CH_2 - CH_2 + I^- + H_2O$ (O) | $H_2O$ | B > A | | | $kA$ | 0 | 1.50 | -2 | | | | (2)(3) |
| | | | | | | | 5 | 3.05 | -2 | | | | |
| | | | | | | | 10 | 6.40 | -2 | 22.2 | 8.5 | 15 | |
| | | D1 64.2 | B > A | | | $kA$ | 0 | 9.9 | -2 | | | | " |
| | | Me 66.3 | B > A | | | $kA$ | 0 | 1.0 | -2 | | | | " |
| .5 | $CH_2{:}CHCHOHCH_2Cl + OH^- \rightarrow CH_2{:}CHCH - CH_2 + Cl^- + H_2O$ (O) | $H_2O$ | A = B = 0.1 | | | $kAB$ | 0 | 2.82 | -2 | | | | (1) |
| | | | | | | | 25 | 5.0 | -1 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5.1 | $CH_2{:}CHCHOHCH_2Cl \rightarrow CH{:}CHCH - CH_2 + HCl$ (O) | $H_2O$ | 0.1 | | | $kA$ | 70 | 9.2 | -8 | | | | (1) |
| .6 | $CH_2{:}CHCHClCH_2OH + OH^- \rightarrow$ $CH_2{:}CHCH - CH_2 + Cl^- + H_2O$ (O) | $H_2O$ | A = B = 0.1 | | | $kAB$ | 0 | 1.16 | 0 | | | | (1) |
| .7 | $CH_2{:}CHCHClCH_2OH \rightarrow CH_2{:}CHCH - CH_2 + HCl$ (O) | $H_2O$ | 0.1 | | | $kA$ | 30<br>50<br>60<br>70 | 1.25<br>1.56<br>4.7<br>1.13 | -5<br>-4<br>-4<br>-3 | | | | (1) |

## SOLVENTS

Di 55.0 (64.2) = $H_2O$ + 1,4 - dioxane, dielectric constant = (55.0) (64.2)

Me 55.0 (66.3) = $H_2O$ + $CH_3OH$, dielectric constant = 55.0 (66.3)

Et 74 = $H_2O$ + $C_2H_5OH$, dielectric constant = 74

## LITERATURE

(1) R. G. Kadesch, *ACS* 1946, **68**, 46. (2) C. L. McCabe, J. C. Warner, *ACS* 1948, **70**, 4031. (3) J. E. Stevens, C. L. McCabe, J. C. Warner, *ACS* 1948, **70**, 2449. (4) L. O. Winstrom, J. C. Warner, *ACS* 1939, **61**, 1205.

# ELIMINATION

## of Hydrogen halide from quaternary base



Reaction type $ArCOCH_2N\begin{matrix}(CH_3)_2X\\CH_2Ar'\end{matrix} + OR^- \rightarrow ArCOCH\begin{matrix}N(CH_3)_2\\CH_2Ar'\end{matrix} + HOR + X^-$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OH^-$ | $H_2O$ | A = 0.1; B = 0.1 | $kA$ | 37.7 | 4.22 | -6 | (2) |
| | | | 0.05 0.05 | | " | 2.34 | -6 | |
| | | | 0.05 0.1 | | " | 4.62 | -6 | |
| .2 | $C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.1; B = 0.1 | $kA$ | 37.7 | 5.5 | -5 | (2) |
| | | | 0.05 0.05 | | " | 5.3 | -5 | |
| | | | 0.05 0.1 | | " | 7.0 | -5 | |
| | | | 0.025 0.05 | | " | 7.0 | -5 | |
| .3 | $C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OC_2H_5^-$ | $C_2H_5OH$ | A = 0.1; B = 0.1 | $kA$ | 37.7 | 1.65 | -4 | (2) |
| | | | 0.5 0.1 - 0.5 | | 37.7 | 1.77 | -4 | |
| .4 | $C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OC_3H_7^-$ | $C_3H_7OH$ | A = 0.05; B = 0.05 | $kA$ | 37.7 | 1.85 | -4 | (2) |
| | | | 0.1 0.1 | | " | 1.87 | -4 | |
| | | | 0.05 0.1 | | " | 2.1 | -4 | |
| .5 | $C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH(CH_3)_2^-$ | $(CH_3)_2CHOH$ | A = 0.1; B = 0.1 | $kA$ | 37.7 | 4.03 | -4 | (2) |
| | | | 0.05 0.05 | | " | 4.23 | -4 | |
| | | | 0.05 0.1 | | " | 4.58 | -4 | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .6 | $C_6H_5COCH_2N(m\text{-}CH_2C_6H_4OCH_3)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 6.5 | -5 | (2) |
| .7 | $C_6H_5COCH_2N(p\text{-}CH_2C_6H_4OCH_3)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 5.3 | -5 | (2) (1) |
| .8 | $C_6H_5COCH_2N(o\text{-}CH_2C_6H_4NO_2)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 16.4 | 1.78 | -3 | (2) |
| .9 | $C_6H_5COCH_2N(m\text{-}CH_2C_6H_4NO_2)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 16.4 | 6.53 | -3 | (2) |
| .10 | $C_6H_5COCH_2N(p\text{-}CH_2C_6H_4NO_2)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 16.4 | 1.25 | -4 | (2) |
| .11 | $C_6H_5COCH_2N(o\text{-}CH_2C_6H_4Cl)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 16.4 | 6.12 | -5 | (2) |
| .12 | $C_6H_5COCH_2N(m\text{-}CH_2C_6H_4Cl)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 1.70 | -4 | (2) |
| .13 | $C_6H_5COCH_2N(p\text{-}CH_2C_6H_4Cl)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 1.94 | -4 | (2) |
| .14 | $C_6H_5COCH_2N(o\text{-}CH_2C_6H_4Br)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 16.4 | 8.18 | -5 | (2) |
| .15 | $C_6H_5COCH_2N(m\text{-}CH_2C_6H_4Br)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 1.46 | -4 | (2) |
| .16 | $C_6H_5COCH_2N(p\text{-}CH_2C_6H_4Br)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 2.00 | -4 | (2) |
| .17 | $C_6H_5COCH_2N(o\text{-}CH_2C_6H_4I)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 16.4 | 1.38 | -4 | (2) |
| .18 | $C_6H_5COCH_2N(m\text{-}CH_2C_6H_4I)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 1.33 | -4 | (2) |
| .19 | $C_6H_5COCH_2N(p\text{-}CH_2C_6H_4I)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 2.27 | -4 | (2) |
| .20 | $p\text{-}CH_3C_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $kA$ | 37.7 | 7.68 | -5 | (1) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|
| .21 | $p$-$ClC_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $k$A | 37.7 | 5.65 | -5 | (1) |
| .22 | $m$-$BrC_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $k$A | 37.7 | 1.46 | -4 | (2) |
| .23 | $p$-$IC_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$ | $CH_3OH$ | A = 0.05; B = 0.1 | $k$A | 37.7 | 5.46 | -5 | (1) |

## LITERATURE

(1) J. L. Dunn, T. S. Stevens, *CSL* **1932**, 1926.

(2) T. Thomson, T. S. Stevens, *CSL* **1932**, 55.

# ELIMINATION

## $CO_2$ from aliphatic carboxylate

Reaction type $RCOO^- + H_2O \rightarrow RH + HCO_3^-$

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CCl_3COO^- + H_2O \rightarrow CHCl_3 + HCO_3^-$ | $H_2O$ | 0.5 | $k$ A | 44.0 | 2.19 | −7 | | | |
| | | | | | 76.4 | 4.19 | −5 | | | |
| | | | | | 99.8 | 1.32 | −3 | 36.6 | 3.8 | 18 |
| .2 | $CBr_3COO^- + H_2O \rightarrow CHBr_3 + HCO_3^-$ | $H_2O$ | 0.5 | $k$ A | 60.3 | 2.29 | −4 | | | |
| | | | | | 76.4 | 1.16 | −3 | 24.1 | 1.8 | 12 |
| .3 | $C_6H_5C{:}COOO^- + H_2O \rightarrow C_6H_5C{:}CH + HCO_3^-$ | $H_2O$ | 0.5 | $k$ A | 87.0 | 4.7 | −6 | | | |
| | | | | | 125.7 | 3.67 | −4 | 31.5 | 8.5 | 13 |

## COMMENTS

(.3) $k$ at 87.0°C from initial rate; competing hydrogenation interferes at low temperatures.

## LITERATURE

R. A. Fairclough, *CSL* 1938, 1186.



942151 O—51——29

# DISSOCIATION

## N oxides

*Gas phase*

Amounts are in mm Hg.
Rates aee in mm Hg per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|
| .1 | $N_2O_4 \rightarrow 2\ NO_2$ | 132 | $kA$ | 1 | 4.5 | + 3 | |
| | | 156 | | " | 5.0 | + 3 | |
| | | 260 | | " | 7.0 | + 3 | |
| | | 162 | | 25 | 4.4 | + 4 | |
| | | 260 | | " | 4.8 | + 4 | |
| | | 668 | | " | 6.0 | + 4 | |
| | | 235 | | 30 | 5.5 | + 4 | |
| | | 260 | | " | 6.7 | + 4 | |
| | | 342 | | " | 7.5 | + 4 | 14 |

## COMMENTS

Sound dispersion measurements. Data cover a frequency range 9 - 450 kilocycles /sec, at relatively few wave lengths, and are believed to be independent of error due to sound absorption. Data of ([5]) consistent with previous estimates ([1,2,3]). Sound dispersion due to lag in establishing thermal equilibrium between translation or rotation and vibration may modify the above interpretation ([4]). $k$ falls with falling pressure especially at low pressure.

## LITERATURE

([1]) P.D.Brass, R.C.Tolman, *ACS* 1932, **54**, 1003.
([2]) E.Grüneisen, E.Goens, Ann. Physik 1923, **72**, 193.
([3]) G.B.Kistiakowsky, W.T.Richards, *ACS* 1930, **52**, 4661.
([4]) H.O.Kneser, O.Gauler, *PZ* 1936, **37**, 627.
([5]) W.T.Richards, J.A.Reid, *JCP* 1933, **1**, 114.

# DISSOCIATION

## Dicarboxylate → Anhydride + Aldehyde

Rate measured $+\Delta p$

*Gas phase*

Amounts are in mm Hg.

Rates are in mm Hg per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .1 | $(CH_3COO)_2CH_2 \rightarrow (CH_3CO)_2O + HCHO$ | 0.34 | $k$ A | 279 | 3.28 | -4 | | | |
| | | 0.14 - 0.52 | | 296.5 | 7.14 | -4 | | | |
| | | 0.22 - 0.32 | | 304.0 | 1.18 | -3 | | | |
| | | 0.22 - 0.37 | | 312.1 | 1.95 | -3 | | | |
| | | 0.14 - 0.90 | | 316.5 | 2.25 | -3 | 32.9 | 2 | 10 |
| .2 | $(CH_3COO)_2CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CHO$ | 0.18 - 0.80 | $k$ A | 236 | 2.3 | -4 | | | |
| | | | | 246 | 2.7 | -4 | | | |
| | | | | 260 | 1.0 | -3 | | | |
| | | | | 267 | 1.1 | -3 | | | |
| | | | | 278 | 2.5 | -3 | | | |
| | | | | 285 | 3.2 | -3 | | | |
| | | | | 297 | 7.6 | -3 | 32.9 | 2 | 10 |
| .3 | $(CH_3COO)_2CHCl_3 \rightarrow (CH_3CO)_2O + CCl_3CHO$ | 263 - 547 | $k$ A | 230 | 5.5 | -5 | | | |
| | | 200 - 281 | | 240 | 1.15 | -4 | | | |
| | | 174 - 363 | | 250 | 1.90 | -4 | | | |
| | | 172 - 390 | | 260 | 3.50 | -4 | | | |
| | | 218 - 273 | | 270 | 6.45 | -4 | | | |
| | | 50 - 362 | | 280 | 1.23 | -3 | | | |
| | | 89 - 268 | | 290 | 2.10 | -3 | 33.0 | 1.3 | 10 |
| .4 | $(CH_3COO)_2CH{:}CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CH{:}CHCHO$ | 122 - 421 | $k$ A | 219 | 3.5 | -4 | | | |
| | | 169 - 341 | | 230 | 6.3 | -4 | | | |
| | | 264 - 341 | | 240 | 1.15 | -3 | | | |

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .4 | $(CH_3COO)_2CH{:}CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CH{:}CHCHO$ | 197 - 251 | $k$ A | 249 | 2.40 | -3 | | | |
| | *(continued)* | 96 - 513 | | 260 | 3.70 | -3 | | | |
| | | 106 - 235 | | 270 | 6.9 | -3 | | | |
| | | 77 - 187 | | 280 | 1.30 | -2 | 33.0 | 1.3 | 11 |
| .5 | $(CH_3COO)_2CHC_3H_7 \rightarrow (CH_3CO)_2O + C_3H_7CHO$ | 269 | $k$ A | 211.4 | 3.94 | -5 | | | |
| | | 128 | | 227 | 1.28 | -4 | | | |
| | | 120 | | 244.8 | 3.86 | -4 | | | |
| | | 213 | | 263 | 1.07 | -3 | | | |
| | | 125 | | 279 | 1.11 | -3 | 32.9 | 3.2 | 10 |
| .6 | $(CH_3COO)_2CHC_6H_{13} \rightarrow (CH_3CO)_2O + C_6H_{13}CHO$ | 88 - 320 | $k$ A | 230 | 1.45 | -4 | | | |
| | | 134 - 219 | | 240 | 2.40 | -4 | | | |
| | | 117 - 256 | | 250 | 4.89 | -4 | | | |
| | | 184 - 344 | | 260 | 9.0 | -4 | | | |
| | | 130 - 271 | | 270 | 1.70 | -3 | | | |
| | | 286 - 316 | | 280 | 2.76 | -3 | | | |
| | | 133 - 447 | | 290 | 5.20 | -3 | 33.0 | 3.0 | 10 |
| .7 | $(CH_3COO)_2CHC_6H_5 \rightarrow (CH_3CO)_2O + C_6H_5CHO$ | 20 - 400 | $k$ A | 220 | 4.0 | -4 | | | |
| | | | | 230 | 6.3 | -4 | | | |
| | | | | 240 | 1.18 | -3 | | | |
| | | | | 250 | 2.30 | -3 | | | |
| | | | | 260 | 4.40 | -3 | | | |
| | | | | 280 | 7.40 | -3 | | | |
| | | | | 290 | 9.11 | -3 | 33.0 | 1.3 | 11 |
| .8 | $(CH_3COO)_2CH(o\text{-}C_6H_4Cl) \rightarrow (CH_3CO)_2O + o\text{-}ClC_6H_4CHO$ | 100 - 500 | $k$ A | 230 | 6.6 | -4 | | | |
| | | | | 240 | 1.08 | -3 | | | |
| | | | | 250 | 1.85 | -3 | | | |
| | | | | 260 | 2.90 | -3 | | | |

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .8 | $(CH_3COO)_2CH(o\text{-}C_6H_4Cl) \rightarrow (CH_3CO)_2O + o\text{-}ClC_6H_4CHO$ | 100 - 500 | $k$ A | 270 | 6.30 | -3 | | | |
| | *(continued)* | | | 280 | 1.00 | -2 | 33.0 | 1.3 | 11 |
| .9 | $(CH_3COO)_2{:}CH{:}CH \rightarrow (CH_3CO)_2O + CH{:}CHCHO$ | 188 - 338 | $k$ A | 220 | 3.0 | -4 | | | |
| | $O< \;\; | \;\; | >O$ | 230 | 6.0 | -4 | | | |
| | $CH{:}CH \qquad CH{:}CH$ | 122 - 245 | | 240 | 1.05 | -3 | | | |
| | | 104 - 521 | | 250 | 1.90 | -3 | | | |
| | | 162 - 330 | | 260 | 3.50 | -3 | | | |
| | | 159 - 416 | | 270 | 7.0 | -3 | | | |
| | | 72 - 290 | | 280 | 1.20 | -2 | 33.0 | 1.3 | 11 |
| .10 | $(CH_3COO)_2HCCH(OCOCH_3)_2 \rightarrow 2(CH_3CO)_2O + OCHCHO$ | | $k$ A | 265 | 2.12 | -4 | | | |
| | | | | 275 | 4.5 | -4 | | | |
| | | | | 284 | 8.0 | -4 | | | |
| | | | | 295 | 1.58 | -3 | | | |
| | | | | 310 | 4.08 | -3 | 39.2 | 1.8 | 12 |
| .11 | $(C_2H_5COO)_2CH_2 \rightarrow (C_2H_5CO)_2O + HCHO$ | 50 - 2300 | $k$ A | 220 - 305 | | | 33 | 1.7 | 9 |
| .12 | $(C_2H_5COO)_2CHCH_3 \rightarrow (C_2H_5CO)_2O + CH_3CHO$ | 95 | $k$ A | 221 | 7.0 | -5 | | | |
| | | 63 | | 229.2 | 1.24 | -4 | | | |
| | | 155 | | 238.4 | 2.19 | -4 | | | |
| | | 62 | | 244.3 | 3.10 | -4 | | | |
| | | 317 | | 254.4 | 5.35 | -4 | | | |
| | | 290 | | 265 | 9.10 | -4 | 32.9 | 2.5 | 10 |
| .13 | $(C_3H_7COO)_2CHCH_3 \rightarrow (C_3H_7CO)_2O + CH_3CHO$ | 32 - 182 | $k$ A | 222 | 4.5 | -5 | | | |
| | | 90 | | 240 | 1.80 | -4 | | | |
| | | 105 | | 253 | 4.25 | -4 | | | |
| | | 36 - 100 | | 266 | 8.5 | -4 | | | |
| | | 144 - 273 | | 290 | 2.6 | -3 | 33.0 | 1.8 | 10 |

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .14 | $(C_3H_7COO)_2CHCCl_3 \rightarrow (C_3H_7CO)_2O + CCl_3CHO$ | 53 - 213 | $k$ A | 240 | 1.4 | -4 | | | |
| | | 78 - 115 | | 250 | 2.05 | -4 | | | |
| | | 114 - 144 | | 260 | 4.25 | -4 | | | |
| | | 43 - 253 | | 270 | 9.0 | -4 | | | |
| | | 156 - 221 | | 280 | 1.40 | -3 | | | |
| | | 188 - 242 | | 290 | 2.50 | -3 | 33.0 | 1.3 | 10 |
| .15 | $(C_3H_7COO)_2CHC_6H_5 \rightarrow (C_3H_7CO)_2O + C_6H_5CHO$ | 100 - 500 | $k$ A | 230 | 7.0 | -4 | | | |
| | | | | 240 | 1.41 | -3 | | | |
| | | | | 250 | 2.35 | -3 | | | |
| | | | | 260 | 3.84 | -3 | | | |
| | | | | 270 | 6.40 | -3 | | | |
| | | | | 280 | 1.00 | -2 | 33.0 | 1.3 | 11 |

## COMMENTS

Proof of homogeneity given by packing. Final pressure change in agreement with theoretical equation. (.11) Reversible, but secondary decomposition of HCHO precludes equilibrium determination and reduces precision of forward rates.

## LITERATURE

C. C. Coffin, *CJR*[B] 1931, 5, 636. J. R. Dacey, C. C. Coffin, *CJR*[B] 1932, 6, 417. C. C. Coffin, W. B. Beazley, *CJR*[B] 1937, 15, 229. C. C. Coffin, J. R. Dacey, N. A. D. Parlee, *CJR*[B] 1937, 15, 247. N. A. D. Parlee, J. R. Dacey, C. C. Coffin, *CJR*[B] 1937, 15, 254. J. R. Dacey, C. C. Coffin, *CJR*[B] 1937, 15, 260. J. R. Dacey, C. C. Coffin, *JCP* 1939, 7, 315. N. A. D. Parlee, J. C. Arnell, C. C. Coffin, *CJR*[B] 1940, 18, 223. J. C. Cornell, J. R. Dacey, C. C. Coffin,, *CJR*[B] 1940, 18, 410.

# DECOMPOSITION

## Aldehyde hydrate

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH(OH)_2 \rightarrow CH_3CHO + H_2O$ | $(CH_3)_2CO$ 91 % + $H_2O$ 9 % | 1.3 wt % | X = | | $k\,A[X]$ | | | |
| | | | | HCOOH | 0 - 0.002 | | 25 | 1.67 | 0 |
| | | | | $CH_3COOH$ | 0 - 0.006 | | " | 7.37 | −1 |
| | | | | $C_2H_5COOH$ | 0 - 0.005 | | " | 6.91 | −1 |
| | | | | $CH_2ClCOOH$ | 0 - 0.0006 | | " | 5.60 | 0 |
| | | | | $CHCl_2COOH$ | 0 - 0.0002 | | " | 2.96 | +1 |
| | | | | $C_6H_5COOH$ | 0 - 0.001 | | " | 2.27 | 0 |
| | | | | $C_6H_5OH$ | 0 - 2.2 | | " | 6.95 | −4 |
| | | | | o-$NO_2C_6H_4OH$ | 0 - 0.2 | | " | 1.28 | −2 |
| | | | | 2, 4-$(NO_2)_2C_6H_3OH$ | 0 - 0.001 | | " | 3.49 | 0 |
| | | | | $CH_3NO_2$ | 0 - 4.3 | | " | 3.22 | −5 |
| | | | | $C_2H_5NO_2$ | 0 - 3.3 | | " | 1.07 | −4 |

## COMMENTS

Dilatometric measurements. X is the undissociated part of the catalyst; a correction allowing for the dissociation was deducted from the observed $k'$, by $k = k'(-0.4K^{0.225})$.

Selected data only are tabulated; further data for a series of acids, phenols, and amides, in the original. Reverse reaction, see 612.410.

## LITERATURE

R. P. Bell, W. C. E. Higginson, *PRS*[A] 1949, 197, 141.

# DECOMPOSITION

## Cyanohydrins



Reaction type **ArCH(OH)CN → ArCHO + HCN**

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CH(OH)CN$ | $C_2H_5OH$ | $C_5H_5N.C_6H_5COOH$ | 0.01 | $kA$ | 20 | 8.7 | -11 |
| .2 | $p$-$CH_3C_6H_4CH(OH)CN$ | $C_2H_5OH$ | $C_5H_5N.C_6H_5COOH$ | 0.01 | $kA$ | 20 | 8.8 | -11 |
| .3 | $p$-$C_2H_5C_6H_4CH(OH)CN$ | $C_2H_5OH$ | $C_5H_5N.C_6H_5COOH$ | 0.01 | $kA$ | 20 | 8.2 | -11 |
| .4 | $p$-$(CH_3)_2CHC_6H_4CH(OH)CN$ | $C_2H_5OH$ | $C_5H_5N.C_6H_5COOH$ | 0.01 | $kA$ | 20 | 6.8 | -11 |
| .5 | $p$-$(CH_3)_3CC_6H_4CH(OH)CN$ | $C_2H_5OH$ | $C_5H_5N.C_6H_5COOH$ | 0.01 | $kA$ | 20 | 6.8 | -11 |

### COMMENTS

Reverse reaction, see 612.415.

### LITERATURE

J. W. Baker, M. L. Hemming, *CSL* **1942**, 191.

# DECOMPOSITION

## Diacetone alcohol dissociation

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COCH_2C(CH_3)_2OH \rightarrow 2(CH_3)_2CO$ | $H_2O$ | ~ 0.1 | NaOH | 0.01 | $kA$ | 20 | 4.79 | -5 | | * | ([7]) |
| | | | | | 0.06 | | " | 3.02 | -4 | | | |
| | | | | | 0.10 | | " | 5.15 | -4 | | | |
| | | | | | 0.01 | | 25 | 7.50 | -5 | | | " |
| | | | | | 0.06 | | " | 4.73 | -4 | | | |
| | | | | | 0.10 | | " | 8.06 | -4 | | | |
| | | | | | 0.01 | | 30 | 1.25 | -4 | | | " |
| | | | | | 0.06 | | " | 7.75 | -4 | | | |
| | | | | | 0.10 | | " | 1.34 | -3 | | | |
| | | | | | 0.01 | | 35 | 2.03 | -4 | | | " |
| | | | | | 0.06 | | " | 1.27 | -3 | | | |
| | | | | | 0.10 | | " | 2.17 | -3 | 18 | | |
| | | $H_2O$ | ~ 0.1 | NaOH | 0.05 | $kA$ | | | | | | |
| | | | | + NaCl | 0.05 | | 20 | 2.47 | -4 | | | " |
| | | | | | 0.55 | | " | 2.15 | -4 | | | |
| | | | | | 0.95 | | " | 1.95 | -4 | | | |
| | | | | | 0.05 | | 25 | 3.84 | -4 | | | " |
| | | | | | 0.55 | | " | 3.29 | -4 | | | |
| | | | | | 0.95 | | " | 2.98 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COCH_2C(CH_3)_2OH \rightarrow 2(CH_3)_2CO$ *(continued)* | | | | 0.05 | | 30 | 6.29 | -4 | | | ([7]) |
| | | | | | 0.55 | | " | 5.53 | -4 | | | |
| | | | | | 0.95 | | " | 5.08 | -4 | | | |
| | | | | | 0.05 | | 35 | 1.04 | -3 | | | " |
| | | | | | 0.55 | | " | 8.90 | -4 | | | |
| | | | | | 0.95 | | " | 8.01 | -4 | | | |
| | | $H_2O + CH_3OH$ 0 % | ~ 0.1 | NaOH | 0.10 | *k* A | 20 | 5.15 | -4 | | | " |
| | | 20 | | | | | " | 2.76 | -4 | | | |
| | | 60 | | | | | " | 7.97 | -5 | | | |
| | | 0 | | " | " | | 25 | 8.08 | -4 | | | " |
| | | 20 | | | | | " | 4.45 | -4 | | | |
| | | 60 | | | | | " | 1.49 | -4 | | | |
| | | 0 | | " | " | | 30 | 1.34 | -3 | | | " |
| | | 20 | | | | | " | 7.71 | -4 | | | |
| | | 60 | | | | | " | 2.44 | -4 | | | |
| | | 0 | | " | " | | 35 | 2.17 | -3 | | | |
| | | 20 | | | | | " | 1.29 | -3 | | | |
| | | 60 | | | | | " | 4.71 | -4 | | | |
| | | $H_2O$ | ~ 0.1 | NaOH ~ | 0.1 | *k* A | | | | | | |
| | | | | + NaCl | 0.0 | | 25 | 7.54 | -4 | | * | ([1]) |
| | | | | | 1.0 | | " | 5.72 | -4 | | | |
| | | | | | 3.0 | | " | 3.86 | -4 | | | |
| | | | | | 6.0 | | " | 3.00 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COCH_2C(CH_3)_2OH \rightarrow 2(CH_3)_2CO$ *(continued)* | | | KOH ~ | 0.1 | $kA$ | | | | | | |
| | | | | + KCl | 0.0 | | 25 | 7.82 | -4 | | | (1) |
| | | | | | 1.0 | | " | 6.36 | -4 | | | |
| | | | | | 3.0 | | " | 4.84 | -4 | | | |
| | | $H_2O$ | 0.43 | NaOH | 0.0023 | $kA$ | 25.2 | 1.72 | -5 | | * | (4) |
| | | | | | 0.0094 | | " | 8.50 | -5 | | | |
| | | | | | 0.018 | | " | 1.66 | -4 | | | |
| | | | | | 0.045 | | " | 4.32 | -4 | | | |
| | | | | | 0.094 | | " | 8.3 | -4 | | | |
| | | $H_2O$ | | NaOH | 0.090 | $kA$ | 15.0 | 3.50 | -4 | | | (3) |
| | | $D_2O$ 99 % | | NaOH | 0.091 | " | 15.0 | 3.97 | -4 | | | " |
| | | | | | 0.133 | | " | 6.40 | -4 | | | |
| | | $H_2O + C_2H_5OH$ 50 % | 0.0805 | | | | | | | | | |
| | | $CH_3NH_2$ | 0.060 + $CH_3NH_2.HCl$ | | 0.020 | $kA$ | 25 | 4.78 | -5 | | | (8) |
| | | | 0.090 | | 0.030 | | " | 6.44 | -5 | | | |
| | | | 0.150 | | 0.050 | | " | 1.03 | -4 | | | |
| | | $H_2O + CH_3OH$ 75 % | | | | | | | | | | |
| | | $CH_3NH_2$ | 0.045 + $CH_3NH_2.HCl$ | | 0.135 | $kA$ | 25 | 4.16 | -5 | | | " |
| | | | 0.075 | | 0.150 | | " | 6.56 | -5 | | | |
| | | | 0.120 | | 0.040 | | " | 1.01 | -4 | | | |
| | | | 0.150 | | 0.030 | | " | 1.17 | -4 | | | |

## COMMENTS

Data of (7)(1)(4)(8) from dilatometric, data of (3) from viscosity measurements. The base of logarithms used is explicitly stated by (7) to be 10; consequently, these data have been converted to natural logarithms. By comparison with the converted data of (7), the data of (1) and (4) must also have been to the basis 10, and have been converted accordingly. Agreement of the converted $k$ of (1) and (4) with (7) is fair. From all data, the rate appears to be very nearly proportional to $[OH^-]$ in the range investigated. Extensive data of $k$ in the presence of NaOH ( + NaF, $Na_2CrO_4^-$, $NaNO_2$, $NaNO_3$, NaCl, NaBr, NaI, NaSCN, NaCN, $Na_2CO_3$) and KOH ( + $K_2SO_4$, $K_2CrO_4$, $KNO_2$, $KNO_3$, $KClO_3$, KCl, KBr, KI, KSCN, KCN) at close concentrations, in NaOH, KOH, and LiOH, + salts, and in the presence of KOH + KCl, NaOH + NaCl, LiOH + LiCl at equal total concentrations and varying proportions, and discussions, see original (1). Discussions of the data of (1) from the point of view of ionic strength and dielectric constant effects, see (2). Activation energy calculations on the basis of the data of (7), see (5).

## LITERATURE

(1) G.Akerlöf, *ACS* 1926, **48**, 3046; 1927, **49**, 2960; 1928, **50**, 1272. (2) E.S.Amis, G.Jaffe, R.T.Overman, *ACS* 1944, **66**, 1823. (3) J.C.Hornel, J.A.V.Butler, *CSL* 1936, 1361. (4) K.Koelichen, *ZPC* 1900, **33**, 129. (5) V.K.LaMer, *JCP* 1933, **1**, 289. (6) V.K.LaMer, M.L.Miller, *ACS* 1935, **57**, 2674. (7) G.M.Murphy, *ACS* 1931, **53**, 977.

(8) F.H.Westheimer, W.A.Jones, *ACS* 1941, **63**, 3283.

# DECOMPOSITION

## Bond Unsaturation

## Loss of hydrogen halide

*Gas phase*

Amounts are in mm Hg.
Rate constants are in $sec^{-1}$.

| No. | Reaction | Amount of reactant | Addend (catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_5Br \rightarrow C_2H_4 + HBr$ | 140 - 360 | | | $kA$ | 395 | 5.9 | -4 | | | | * | (7) |
| | | | | | | 405 | 1.1 | -3 | | | | | |
| | | | | | | 420 | 2.5 | -3 | 55 | 3.8 | 14 | | |
| | | 215 - 650 | | | $kA$ | 375 | 3.3 - 5.5 | -4 | | | | * | (5) |
| | | | | | | 388 | 6.6 - 11.7 | -4 | | | | | |
| | | | | | | 402 | 1.67 | -3 | ~ 50 | ~ 1 | 13 | | |
| .1.1 | $C_2H_5Br \rightarrow C_2H_4 + HBr$ | 190 | $Br_2$ | 6.2 | $kA$ | 400 | 1.0 | -3 | | | | * | (2) |
| | | | | 14 | | " | 1.6 | -3 | | | | | |
| | | | | 25 | | " | 2.5 | -3 | 22 | | | | |
| .2 | $C_3H_7Br \rightarrow C_3H_6 + HBr$ | 54 | | | $kA$ | 353.5 | 4.5 | -4 | | | | * | (5) |
| | | 215 | | | | " | 1.05 | -3 | | | | | |
| | | 274 | | | | " | 9.7 | -4 | | | | | |
| .3 | $(CH_3)_2CHBr \rightarrow C_3H_6 + HBr$ | 265 | | | $kA$ | 335 | 1.35 | -4 | | | | * | (5) |
| .4 | $(CH_3)_3CCl \rightarrow C_4H_8 + HCl$ | 300 | | | $kA$ | 280 | 8.7 | -4 | | | | * | (5) |
| | | | | | $kA$ | 270 - 372 | | | 46.0 | 1.9 | 14 | | (1) |
| .5 | $(CH_3)_3CBr \rightarrow (CH_3)_2C{:}CH_2 + HBr$ | ~ 100 | | | $kA$ | 237 | 1.0 | -4 | | | | * | (4) |
| | | | | | | 253 | 3.4 | -4 | | | | | |
| | | | | | | 267 | 9.4 | -4 | | | | | |
| | | | | | | 286 | 3.25 | -3 | | | | | |
| | | | | | | 290 | 4.2 | -3 | 40.5 | 2 | 13 | | |



942151 O—51——30

| No. | Reaction | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $(C_2H_5)(CH_3)_2CBr \rightarrow C_5H_{10} + HBr$ | | | | $kA$ | 270 – 372 | | | 46.0 | 4.5 | 14 | | (1) |

## COMMENTS

**General.** All data from manometric measurements. **(.1) (.1.1)** Data of (7) more accurate than (5). The reaction is largely homogeneous but certainly accompanied by wall reaction. Reaction products suppress wall catalysis. $k$ falls at lower pressures, e.g. decreases to 50 % under 20 mm at 395°C, to 35 % at 405°C (7). Traces of Hg retard the reaction. $N_2$ and $H_2$ decrease $k$ at low pressures (6). NO has no effect. For the $Br_2$-catalyzed reaction (2), roughly $k \sim [Br_2]^{1/2}$. See further (3). **(.2)** No evidence for first order. **(.3) (.4)** $k$ calculated from half-times assuming first order. **(.5)** Selected points. Proof of homogeneity given. **(.6)** Assuming $E$ to be the same as for reaction (.4).

## LITERATURE

(1) D.Brearly, G.B.Kistiakowsky, C.H.Stauffer, *ACS* 1936, **58**, 43. (2) F.Daniels, P.L.Veltman, *JCP* 1939, **7**, 756. (3) P.Fugassi, F.Daniels, *ACS* 1938, **60**, 771. (4) G.B.Kistiakowsky, C.H.Stauffer, *ACS* **59**, 165, 1937. (5) E.T.Lessig, *JPC* 1932, **36**, 2325. (6) E.L.Vernon, F.Daniels, *ACS* 1932, **54**, 2563. (7) E.L.Vernon, F.Daniels, *ACS* 1933, **55**, 922.

# DECOMPOSITION

## Bond Unsaturation

## Loss of halogen molecule

*Gas phase*

Mass-action in M/l.
Rates in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_2ClCH_2Cl \rightarrow C_2H_4 + Cl_2$ | 355 mm | $kA$ | 360 | 1.67 | -4 | | * | (3) |
| .2 | $CH_2BrCH_2Br \rightarrow C_2H_4 + Br_2$ | 355 mm | $kA$ | 360 | 1.15 | -3 | | * | (3) |
| .3 | $CH_2ICH_2I \rightarrow C_2H_4 + I_2$ | | $kA + k'A[I_2]^{1/2}$ | 205 | $k$ 9.0 | -4 | | * | (1) |
| | | | | " | $k'$ 3.1 | -2 | | | |
| | | | | 220 | $k$ 2.4 | -3 | | | |
| | | | | " | $k'$ 7.4 | -2 | | | |
| | | | | 230 | $k$ 4.4 | -3 | 36 | | |
| | | | | " | $k'$ 1.3 | -1 | 29 | | |
| .4 | 2 *rac*-$(C_2H_5)(CH_3)CHI \rightarrow C_4H_{10} + C_4H_8 + I_2$ | 100 - 250 mm | $kA + k'A[I_2]^{1/2}$ | | | | | * | (4) |
| | | | | 238.0 | $k$ 1.3 | -5 | | | |
| | | | | " | $k'$ 7.6 | -4 | | | |
| | | | | 254.0 | $k$ 4.0 | -5 | | | |
| | | | | " | $k'$ 2.12 | -3 | | | |
| | | | | 276.0 | $k$ 1.90 | -4 | 39.4 | | |
| | | | | " | $k'$ 8.36 | -3 | 35.2 | | |

## COMMENTS

(.1) (.2) Manometric measurements; $k$ calculated from half-time. (.3) $k'$ converted from $(\text{mm Hg})^{-1/2}$ to $(\text{M/l})^{-1/2}$ units. Packing (at 205° and 220°) decreases $k$ slightly, increases $k'$ slightly, and increases slightly both $E$ and $E'$. Reaction partly heterogeneous also according to ([2]) who gives rate data at 65° and 75°C. The (manometric) rate of decomposition is said to be best represented by zero order in the initial stage, then by first order, and finally by second order ([2]). (.4) Manometric measurements; $k'$ converted from $(\text{M/ml})^{-1/2}$ to $(\text{M/l})^{-1/2}$ units. Mechanism proposed: $A \rightarrow C_4H_9 + I$ $(k_1)$; $A + I \rightarrow C_4H_9 + I_2$ $(k_2)$; $C_4H_9 + C_4H_9 \rightarrow C_4H_{10} + C_4H_8$ (fast); $(C_4H_9 + C_4H_9 \rightarrow C_8H_{18})$ (fast); $I_2 \rightleftarrows I + I$ $(K)$; $k = k_1$; $k' = k_2K^{1/2}$.

## LITERATURE

([1]) L.B.Arnold, G.B.Kistiakowsky, *JCP* 1933, **1**, 166. ([2]) T.Iredale, L.W.C.Martin, *JPC* 1934, **38**, 365. ([3]) E.T.Lessig, *JPC* 1932, **36**, 2325. ([4]) R.A.Ogg jr., M.Polanyi, *TFS* 1935, **31**, 482.

# DECOMPOSITION
## Bond Unsaturation
## Dehydration

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CHOHCH_2CHO \rightarrow$ *trans*-$CH_3CH{:}CHCHO + H_2O$ | $H_2O$ | | $HNO_3$ | 0.478 | $k\,A\,[H^+]$ | 25 | 8.13 | −6 | | * | (4) |
| | | | | | 1.43 | | " | 7.77 | −6 | | | |
| | | | | | 1.905 | | " | 8.28 | −6 | | | |
| | | | | " | 0.482 | | 35 | 2.69 | −5 | | | |
| | | | | | 0.96 | | " | 2.83 | −5 | | | |
| | | | | | 1.86 | | " | 2.78 | −5 | 23.5 | | |
| | | | | $HClO_4$ | 0.569 | | 25 | 6.35 | −6 | | | " |
| | | | | | 0.949 | | " | 6.45 | −6 | | | |
| | | | | | 1.88 | | " | 7.66 | −6 | | | |
| | | | | " | 0.373 | | 35 | 2.43 | −5 | | | |
| | | | | | 0.750 | | " | 2.52 | −5 | | | |
| | | | | | 1.872 | | " | 2.90 | −5 | 24.5 | | |
| .2 | $CH_3CHOHCH_2COOH \rightarrow$ *trans*-$CH_3CH{:}CHCOOH + H_2O$ | $H_2O$ | 0.01 − 0.02 | $HClO_4$ | 1 − 2 | $k\,A\,[H^+]$ | 90.0 | 3.89 | −7 | | * | (3) |
| | | | | | | | 111.3 | 2.78 | −6 | 48.1 | | |
| .3 | $(CH_3)_2COHCH_2CHO \rightarrow (CH_3)_2C{:}CHCHO + H_2O$ | $H_2O$ | | $HNO_3$ | 0.5 − 1 | $k\,A\,[H^+]$ | 20 | 5.00 | −6 | | * | (2) |
| | | | | | | | 25 | 8.88 | −6 | | | |
| | | | | | | | 35 | 3.11 | −5 | 22.4 | | |
| .4 | $C_2H_5CHOHCH_2COOH \rightarrow CH_3CH{:}CHCH_2COOH + H_2O$ | $H_2O$ | 1.0 | NaOH | 1.2 | $k\,A$ | 100 | 3.5 | −7 | | * | (1) |
| .5 | $C_2H_5CHOHCH_2COOH \rightarrow C_2H_5CH{:}CHCOOH + H_2O$ | $H_2O$ | 1.0 | NaOH | 1.2 | $k\,A$ | 100 | 4.0 | −7 | | * | (1) |

## COMMENTS

(.1) $k$ calculated from experimental $k' = k[H^+]$; first order in $[H^+]$ appears approximate. (.2) Reverse reaction, see 622.442. (.3) $KNO_3$, $NaNO_3$ added to total $\mu = 0.5 - 2$. (.4) (.5) Rate constants calculated from the rate of establishment of the equilibrium

$$C_2H_5CH{:}CHCOOH \rightleftarrows CH_3CH{:}CHCH_2COOH$$
$$\rightleftarrows C_2H_5CHOHCH_2COOH \rightleftarrows$$

## LITERATURE

(1) D. J. G. Ives, R. H. Kerlogue, *CSL* 1940, 1362. (2) H. J. Lucas, W. T. Stewart, D. Pressman, *ACS* 1944, 66, 1818. (3) D. Pressman, H. J. Lucas, *ACS* 1939, 61, 2271. (4) S. Winstein, H. J. Lucas, *ACS* 1937, 59, 1461.

# DECOMPOSITION

## Bond Unsaturation

## Elimination of quaternary base

*Liquid phase*

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $[C_6H_5CH_2CH_2N(CH_3)_3]OH \rightarrow C_6H_5CH{:}CH_2 + N(CH_3)_3HOH$ | $H_2O$ | 0.165 - 0.330 | $kA^2$ | 100 | 5.9 | -4 |
| .2 | $[p - NO_2C_6H_4CH_2CH_2N(CH_3)_3]^+ \rightarrow p - NO_2C_6H_4CH{:}CH_2 + N(CH_3)_3H^+$ | $H_2O$ | 0.3 | $kA$ | 100 | 4.0 | -5 |

## COMMENTS

**(.1)** Second order indicates mass action of each of the two ions. **(.2)** Iodide and bromide both decompose following a first-order law, with the same value of $k$; consequently, the rate is that of the decomposition of the quaternary cation. Excess of $N(CH_3)_3HI$ or $N(CH_3)_4I$ has no effect.

## LITERATURE

E. D. Hughes, C. K. Ingold, *CSL* **1933**, 523.

# DECOMPOSITION
## Bond Unsaturation
## Loss of $SO_2$ group

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Medium | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|
| .1 | $CH_2CH{:}CHCH_2 \rightarrow CH_2{:}CHCH{:}CH_2 + SO_2$ (SO2) | pure A | $kA$ | 120 | 2.0 | -4 | |
| | | | | 125 | 2.5 | -4 | |
| | | | | 135 | 7.0 | -4 | 27.3 |
| .2 | $CH_2CH{:}CHCHCH_3 \rightarrow CH_2{:}CHCH{:}CHCH_3 + SO_2$ (SO2) | pure A | $kA$ | 85 | 5.5 | -5 | |
| | | | | 90 | 8.68 | -5 | |
| | | | | 94 | 1.18 | -4 | 19.5 |
| .3 | $CH_2CH{:}C(CH_3)CH_2 \rightarrow CH_2{:}CHC(CH_3){:}CH_2 + SO_2$ (SO2) | pure A | $kA$ | 100 | 1.52 | -5 | |
| | | | | 120 | 1.55 | -4 | |
| | | | | 138 | 1.12 | -3 | 32.9 |

## LITERATURE

L. R. Drake, S. C. Stowe, A. M. Partansky, *ACS* 1946, **68**, 2521.

# REDUCTIVE DECOMPOSITION

*Gas phase*

Rate constants in $sec^{-1}$.

| No. | Reaction | Wall | Amount of reactant | Carrier Gas | Surface/volume ratio (s/v) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $H_2O_2 \rightarrow H_2 + O_2$ | $B_2O_3$ (on pyrex) | 1 - 2 mm Hg | $N_2$ (1 atm) | 7 $cm^{-1}$ | $kA$ | 467 | 1.8 | -1 | | * | (1) |
| | | | | | | | 500 | 5.0 | -1 | | | |
| | | | | | | | 521 | 1.19 | 0 | 40 | | |
| | | | | " | 3 $cm^{-1}$ | " | 467 | 1.1 | -1 | | | " |
| | | | | | | | 500 | 5.0 | -1 | | | |
| | | | | | | | 521 | 1.11 | 0 | 50 | | |
| | | | | $O_2$ (1 atm) | 7 $cm^{-1}$ | " | 500 | 3.8 | -1 | | | " |
| | | | | | | | 542 | 1.6 | 0 | 40 | | |
| | | | | " | 3 $cm^{-1}$ | " | 500 | 2.1 | -1 | | | " |
| | | | | | | | 542 | 3.0 | 0 | | | |
| .2 | $H_2O_2 + H_2 \rightarrow 2\ H_2O$ | $B_2O_3$ (on pyrex) | A = 1 - 2 mm Hg; | $N_2$ ($N_2 + H_2$ = 1 atm) | 3 $cm^{-1}$ | $kA$ | 467 | 1.45 | 0 | | * | (2) |
| | | B (mole fraction) | ~ 0.4 | | " | | | | | 54 | | |
| | | | 0.074 | | | | | | | 64 | | |
| | | | ~ 0.4 | | 7 $cm^{-1}$ | | | | | 37 | | |
| | | | 0.074 | | | | | | | 41 | | |

## COMMENTS

(.1) At least largely homogeneous by the slight effect of $s/v$ between 7 and 3 $cm^{-1}$. $E$ = 40 is by 13 kcal less than $H_2O_2 \rightarrow 2\ OH$; difference possibly attributable to some amount of wall reaction. $E$ = 50 at the lower $s/v$ is closer to $H_2O_2 \rightarrow 2\ OH$. Possibly $E$ = 40 - 50 might correspond to $H_2O_2 \rightarrow H_2O + O$ (35 kcal) + excess activation. The selected data correspond to a flow rate of 0.5 l/min ; no appreciable effect of variation of flow rate.

(.2) Simplified from the expression given in the original, rate law

$$-dA/dt = k_i \frac{k_1A^2B}{k_2A + k_3B + m} \qquad (k_i = \text{initiation})$$

giving, at low $H_2$ ($\lesssim$ 0.4 mole fraction), rate $\sim$ AB, and tending, at increasingly higher $H_2$, towards rate $\sim A^2$.

Actual order in A, between 1 and 2; in $H_2$, not higher than 1, and decreasing with increasing $[H_2]$.

*Surface/volume effects:*

Between $s/v$ = 3 and 7 $cm^{-1}$.

(a) at 467°, at low $H_2$, increase of $s/v$ accelerates
" " " high " " " " decelerates

(b) at 480°, $s/v$ without effect

(c) at 500°, increase of $s/v$ decelerates at all $H_2$.

*Mechanism:*

Initiation partly homogeneous, partly at the wall; termination at the wall.

| | |
|---|---|
| *Initiation* | $H_2O_2 \rightarrow 2\ OH$ |
| | $H_2O_2 + w \rightarrow 2\ OH$ |
| *Propagation* | $OH + H_2 \rightarrow H_2O + H$ |
| | $H + H_2O_2 \rightarrow H_2O + OH$ |
| *Termination* | $H + w$ |
| | $OH + w$ |

## COMMENTS *(continued)*

This mechanism gives the rate law schematized above. Replacement of $H_2$ by an equal proportion of $O_2$ results in from considerable reduction of the amount of $H_2O_2$ decomposed to suppression of decomposition and even occasional over-production of $H_2O_2$; attributed to initiation of the $H_2 + O_2$ reaction by $H_2O_2$.

## LITERATURE

(1) C. K. McLane, *JCP* 1949, **17**, 379.

(2) C. K. McLane, *JCP* 1950, **18**, 972.

# REDUCTIVE DECOMPOSITION

## C oxyhalides



Rate measured $+\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | |
| .1 | $COCl_2 \rightarrow CO + Cl_2$ | 0.0015 - 0.015 | $k\,AM^{1/2}$ | 451 | 3.0 | -1 | 22.9 | 4.18 | 15 | (1) |

## COMMENTS

Reverse reaction see 641.470. The proposed mechanism, $Cl_2 \rightleftarrows 2\,Cl$; $Cl + COCl_2 \rightarrow COCl + Cl_2$; $COCl \rightleftarrows CO + Cl$, is based on analogy with photochemical reactions which seem to rule out $Cl_3$ as intermediate (2).

## LITERATURE

(1) M. Bodenstein, H. Plaut, *ZPC* 1924, **110**, 399.
(2) M. Bodenstein, W. Brenschede, H.J. Schumacher, *ZPC*[B] 1935, **28**, 81; 1938, **40**, 121.

# REDUCTIVE DECOMPOSITION

## N oxides

*Gas phase*

**Homogeneous Reactions**
**541.560**

Rates are in "unit of amount per sec.

| No. | Reaction | Method | Unit of amount | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2N_2O \rightarrow 2N_2 + O_2$ | $p$ | mm Hg | 80 | $k$ A | 665 | 1.2 | -4 | | | | * | (43) |
| | | | | 485 | | " | 4.3 | -4 | | | | | |
| | | | | 970 | | " | 6.5 | -4 | | | | | |
| | | | | 2000 | | " | 1.0 | -3 | | | | | |
| | | | | 5000 | | " | 1.4 | -3 | | | | | |
| | | | | 8000 | | " | 1.6 | -3 | | | | | |
| | | | | 28 | " | 603 | 1.7 | -5 | | | | | (43) |
| | | | | " | | 647 | 8.9 | -5 | | | | | |
| | | | | " | | 697 | 3.5 | -4 | | | | | |
| | | | | 8000 | " | 575 | 8.0 | -5 | | | | | " |
| | | | | " | | 620 | 4.0 | -4 | 53 | 4.2 | 9 | | |
| | | | kg/cm² | 37.43 | " | 585 | 1.5 | -4 | | | | * | (18) |
| | | | | 18.37 | | 602 | 2.4 | -4 | | | | | |
| | | | | 24.54 | | 615 | 4.2 | -2 | | | | | |
| | | | | ~ 0.1 | | 510 - 600 | | | 64.9 | | | | (18) |
| | | | | ~ 0.5 | | 630 - 695 | | | 61.0 | | | | |
| | | | | ~ 40 | | 640 - 725 | | | 53.0 | | | | |
| | | | M/ml | 0.4 - 40 kg/cm² | $k A^{1/2}$ | 585 - 615 | | | 67 | 9.5 | 14 | * | (31) |



942151 O—51——31

| No. | Reaction | Method | Unit of amount | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $2NO \rightarrow N_2 + O_2$ | flow | M/ml | $A \sim 1 - 4$<br>$A/M \sim 0.1 - 1.5$<br>$A + L + M = 1$ atm | $-dA/dt = A^2 \left\{ [a/(b + A/M)M^{1/2}] + [cA/M/(b + A/M)] \right\}$ | | | | | | | | |
| | | | | | | 906 | c 6.0 | 0 | | | | * | (42) |
| | | | | | | 1252 | a 1.15 | 0 | | | | | |
| | | | | | | | b 2.0 | -2 | | | | | |
| | | | | | | | c 1.35 | +3 | | | | | |
| | | | | | | 1639 | a 6.0 | +2 | | | | | |
| | | | | | | | b 7.0 | -2 | | | | | |
| | | | | | | | c 7.9 | +4 | | | | | |
| .3 | $N + O_2 \rightarrow NO + O$ | from .2 | M/ml | | $k$ AB | 1330 | 9.2 | 8 | 25 | | | * | (42) |
| .4 | $O + N_2 \rightarrow NO + N$ | from .2 | M/ml | | $k$ AB | 1330 | 4.0 | 4 | 55 | | | * | (42) |
| .5 | $O + NO \rightarrow O_2 + N$ | from .2 | M/ml | | $k$ AB | 1330 | 6.0 | 7 | 29 | | | * | (42) |
| .6 | $N + NO \rightarrow N_2 + O$ | from .2 | M/ml | | $k$ AB | 1330 | 3.7 | 10 | 7 | | | * | (42) |
| .7 | $2NO \rightarrow NO_2 + N$ | from .2 | M/ml | | $k$ AB | 1330 | 9.5 | 2 | 52 | | | * | (42) |
| .8 | $N + NO_2 \rightarrow 2NO$ | from .2 | M/ml | | $k$ AB | 1330 | 4.1 | 10 | 2 | | | * | (42) |
| .9 | $NO_2 \rightarrow NO + O$ | from .2 | | | $k$ A | 1330 | 4.6 | -1 | 78 | | | * | (42) |
| .10 | $O + NO \rightarrow NO_2$ | from .2 | M/ml | | $k$ AB | 1330 | 8.6 | 7 | 6 | | | * | (42) |
| .11 | $2NO_2 \rightarrow 2NO + O_2$ | $p$ | M/l | 10 - 40<br>mm Hg | $k A^2$ | 319 | 1.0 | 0 | | | | * | (1) |
| | | | | | | 330 | 1.5 | 0 | | | | | |
| | | | | | | 354 | 3.4 | 0 | | | | | |
| | | | | | | 378 | 8.0 | 0 | | | | | |
| | | | | | | 383 | 1.0 | 1 | 26.6 | 6 | 9 | | |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .12 | $2N_2O_5 \rightarrow 4NO_2 + O_2$ | $p(O_2)$ | mm Hg | | $k$ A | | | | | | | | |
| | | | | 0.063 - 0.081 | | 35 | 1.4 | -4 | | | | * | (24) |
| | | | | 0.0010 - 0.0018 | " | 35 | 3.5 | -5 | | | | | |
| | | | | | | 45 | 1.1 | -4 | | | | | |
| | | | | | | 55 | ~ 3 | -4 | | | | | |
| | | | | | | 65 | ~ 7 | -4 | | | | | |
| | | | | 30 - 700 | " | 0 | 7.9 | -7 | | | | * | (5) |
| | | | | | | 15 | 1.0 | -5 | | | | | |
| | | | | | | 25 | 3.3 | -5 | | | | | |
| | | | | | | 35 | 1.3 | -4 | | | | | |
| | | | | | | 45 | 5.0 | -4 | | | | | |
| | | | | | | 65 | 4.9 | -3 | 24.8 | 3.8 | 16 | * | (22) |

## COMMENTS

(.1) Rate constants (from half-lives) given as first-order without implying an actual first order; pressure increase on completion is 46.5 %, not 50 % ([13, 43]); first-order $k$ increase with the pressure ([18, 11]). Activation energy of 53 kcal and frequency factor of $4.2 \times 10^9$ refer to 10 atm pressure (extrapolated); the frequency factor is 100 times too small ([34]). Treatment of the data of ([18]) as of 1.5 order ([31]) gives $k = 9.5 \times 10^{14} e^{-67000/RT}$ $(M/ml)^{-1/2}$ $sec^{-1}$ with a maximum deviation of 15 % between 0.36 and 40 kg/cm$^2$. The reaction is stated to be explosive under 70 atm. NO is present during the reaction ([2]) reaching a maximum at 50 % completion ([26]). Foreign gases accelerate the rate with the following activation efficiencies: $H_2O$ 1.50, $CO_2$ 1.32, $N_2O$ 1.0, $N_2$ 0.24, $O_2$ 0.23 ([43, 14]). Under 0.1 mm Hg in quartz the reaction is heterogeneous ([8]). The reaction is catalyzed by Hg, $Br_2$, and $I_2$ vapors at rates proportional to [Hg], $[Br_2]^{1/2}$, and $[I_2]^{1/2}$ ([43]), indicating reaction over atoms Hg, Br, and I ([37]). Probable atom chain with NO participating. No decision possible between first and 1.5 order. Older reference ([19]). (.2) - (.10) The rate law ([42]) of the overall reaction (.2) is expressible by the rate constants $k$ of the assumed constituent steps (.3) (.5) (.6) (.7) (.10) and $K$ = dissociation constant of $O_2$, with $a = 2k_5K^{1/2}$: $b = k_3/k_6$; $c = 2k_7[1 + (k_6/k_{10})]$. The subscripts of $k$ correspond to the numbers under which the constituent reactions are listed in the table. These $k$ of these elementary steps and of the reverse reactions (.4) (.8) (.9), given under (.3) - (.10), are derived from (.2) and equilibrium data. (.11) Data, converted to M/l and sec, in agreement with the original observed $k$ ([1]); the data tabulated in the book of Kassel ([22]) and of Schumacher are in error owing to unnecessary division by 2, whereas the original rates actually refer to one mole $NO_2$ and not to 2 moles. (.12) The low-pressure data are from ([24]), chosen as representative and in agreement with much of the previous work. High-pressure data are from ([5]), in very good agreement with more recent work. The low-pressure $k$ is related to the high-pressure $k_\infty$ by $k = k_\infty/(1 + aA)$, with $a = 0.0033$ and 0.0065 at 35° and 55°C, respectively. Data of $E$ and the frequency factor ([22]) are weighted averages from several sources. Further literature references, and interpretations, ([3, 4, 5, 6, 7, 9, 10, 12, 15, 16, 17, 21, 23, 25, 28, 29, 30, 32, 33, 35, 36, 38, 39, 40, 41, 44]). See reaction in the liquid phase, 542.560.

## LITERATURE

(1) M. Bodenstein, Ramstetter, *ZPC* 1922, 100, 106. (2) E. Briner, C. Meiner, A. Rothen, *JCC* 1926, 23, 607. (3) F. Daniels, *ACS* 1926, 48, 607. (4) F. Daniels, A.C. Bright, *ACS* 1920, 42, 1131. (5) F. Daniels, E.H. Johnston, *ACS* 1921, 43, 53 and 72. (6) F. Daniels, O. R. Wulf, S. Karrer, *ACS* 1922, 44, 2402. (7) J. H. Hibben, *NAS* 1927, 13, 626. (8) J. H. Hibben, *ACS* 1928, 50, 937. (9) J. H. Hibben, *ACS* 1928, 50, 940. (10) J. H. Hibben, *JPC* 1930, 34, 1387.

(11) C. N. Hinshelwood, *PRS*[A] 1934, 146, 239. (12) C. N. Hinshelwood, The kinetics of chemical change, *Oxford*, 1940. (13) C. N. Hinshelwood, R. E. Burk, *PRS*[A] 1924, 106, 284. (14) C. N. Hinshelwood and Lewis, *PRS*[A] 1938, 168, 441. (15) H. S. Hirst, *JCS* 1925, 127, 657. (16) H. S. Hirst, E. K. Rideal, *PRS*[A] 1925, 109, 526. (17) J. Hunt, F. Daniels, *ACS* 1925, 47, 1602. (18) E. Hunter, *PRS*[A] 1934, 144, 386. (19) M. A. Hunter, *ZPC* 1905, 53, 441. (20) K. Jellinek, *ZAC* 1906, 49, 229.

(21) L.S. Kassel, *ACS* 1929, 51, 54. (22) L.S. Kassel, Kinetics of homogeneous gas reactions, New York, 1932. (23) E. F. Linhorst, J. H. Hodges, *NAS* 1931, 17, 28. (24) E. F. Linhorst, J. H. Hodges, *ACS* 1934, 56, 836. (25) A. G. Loomis, D. F. Smith, *ACS* 1926, 50, 1864. (26) F. F. Musgrave, C. N. Hinshelwood, *PRS*[A] 1932, 135, 25. (27) W. Nerst, *ZAC* 1906, 49, 213. (28) M.E. Nordberg, *Thesis, California Inst. of Techn.*, 1928. (29) R.G.W. Norrish, *Nature*, 1927, 119, 123. (30) R. A. Ogg, Jr., *JCP* 1947, 15, 337.

(31) R. N. Pease, *JCP* 1939, 7, 749. (32) H.C. Ramsperger, M.E. Nordberg, R. C. Tolman, *NAS* 1929, 15, 453. (33) H. C. Ramsperger, R. C. Tolman, *NAS* 1929, 16, 129. (34) H. C. Ramsperger, G. Waddington, *PM* 1931, 17, 103. (35) F. O. Rice, D. Getz, *JPC* 1927, 31, 1572. (36) F. O. Rice, H. C. Urey, R. N. Washburn, *ACS* 1928, 50, 2402. (37) H. J. Schumacher, *ZAC* 1937, 50, 483. (38) H. J. Schumacher, G. Sprenger, *ZPC*[A] 1929, 140, 281. (39) H. J. Schumacher, G. Sprenger, *NAS* 1930, 16, 129. (40) G. Sprenger, *ZPC*[A] 1928, 136, 49.

## LITERATURE *(continued)*

(41) H. A. Taylor, *ACS* 1926, **48**, 577. (42) K. Vetter, *IEC* 1949, **53**, 369; 376. (43) M. Volmer et al. *ZPC*[B] 1930, **8**, 141; 1930, **10**, 414; 1931, **19**, 85, 89; 1933, **21**, 257; 1934, **25**, 81. (44) E. C. White, R.C. Tolman, *ACS* 1925, **47**, 1240.

# REDUCTIVE DECOMPOSITION

## Ozone



Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | Literature |
|---|---|---|---|---|---|---|---|---|---|
| | | $10^3[O_3]$ | $10^4[O_2]$ | | | $k^o$ | $n$ | | |
| .1 | $2\,O_3 \rightarrow 3\,O_2$ | | | $k\,A^2$ | | | | | (2) |
| | | 4.6 | 0.89 | | 70 | 5 | -3 | | |
| | | 6.0 | 1.5 | | 80 | 1.4 | -2 | | |
| | | 5.3 | 200 | | " | 1.4 | -2 | | |
| | | 6.4 | 5.6 | | 90 | 3.5 | -2 | | |
| | | 5.3 | 230 | | " | 4.5 | -2 | | |
| | | 3.2 | 5.0 | | 100 | 8.6 | -2 | 24.4 | |
| | | 4.5 | 270 | | " | 1.3 | -1 | 28.5 | |

## COMMENTS

Selected data from ([2]), deemed most reliable from the point of view of absence of impurities (organic matter, Hg, $H_2$, $N_2$), and in good agreement with previous work where the ranges overlap. All $k$ are initial; $k$ increases steadily in each run and is slightly (~ 10 %) increased by packing. Foreign gases accelerate the reaction in the order $CO_2 > N_2 > He$.

The value of $E = 24.4$ is valid for pure $O_3$; at high $[O_2]$ it rises to 28.5.

The chain mechanism proposed, (1) $O_3 + O_3 \rightarrow 3\ O_2^*$; (2) $O_2^* + O_3 \rightarrow 2\ O_2 + O$; (3) $O + O_3 \rightarrow 2\ O_2^{**}$; (4) $O + O_2 + M \rightarrow O_3 + M$; (5) $O_2^{**} + O_3 \rightarrow 2\ O_2 + O$; (6) $O_2^{**} + O_3 \rightarrow O_2 + O_3$; (7) $O_2^{**} + O_2 \rightarrow 2\ O_2$, gives, for $[O_2] = 0$, $-d[O_3]/dt = k_1[O_3]^2$, and for $[O_2] \gg [O_3]$, at high temperature, $-d[O_3]/dt = (k_2 k_3/k_4)\ [O_3]^2/[O_2]$ ([3, 4, 5, 7, 8]). From the photochemical reaction ([6]), giving $k_4/k_5$ and $(k_6/k_5) + (k_7/k_5)$ and their temperature dependence, $k_1 = 1.7 \times 10^{13}\ e^{-24400/RT}$ and $k_2 = 1.83 \times 10^{14} e^{-28500/RT}$.

## LITERATURE

([1]) E. J. Bowen, E. A. Moelwyn-Hughes, C. N. Hinshelwood, *PRS*[A] 1931, **134**, 211.

([2]) A. Glissmann, H. J. Schumacher, *ZPC*[B] 1933, **21**, 323. ([3]) S. T. Jahn, *ZAC* 1906, **48**, 260. ([4]) E. P. Perman, R. H. Greaves, *PRS*[A] 1908, **80**, 353.

([5]) E.H.Riesenfeld, H.J.Schumacher, *ZPC* 1928, **138**, 268. ([6]) H.J.Schumacher, *ZPC*[B] 1932, **17**, 405, 417; *ACS* 1930, **52**, 2377. ([7]) O. R. Wulf, R. C. Tolman, *ACS* 1927, **49**, 1183, 1202, 1650. ([8]) O. R. Wulf, *ACS* 1932, **54**, 156.

# REDUCTIVE DECOMPOSITION

## Halogen oxides



Rate and rate constants are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|
| .1 | $2\ F_2O \rightarrow 2\ F_2 + O_2$ | 50 - 800 mm Hg | $kA^2$ | 250<br>260<br>270 | 1.39<br>2.86<br>5.71 | -2<br>-2<br>-2 | 39 ± 3 |

### COMMENTS

Unimolecular reaction in second-order range requiring 3 oscillators and diameter $4.5 \times 10^{-8}$ cm. Relative efficiencies for activation:

| $F_2O$ | $F_2$ | $O_2$ | $N_2$ | $SiF_4$ | Ar | He |
|---|---|---|---|---|---|---|
| 1.0 | 1.1 | 1.1 | 1.0 | 0.88 | 0.52 | 0.40 |

### LITERATURE

W. Kobitz, H. J. Schumacher, *ZPC*[B] 1934, 25, 283.

# REDUCTIVE DECOMPOSITION

## N oxides

*Liquid phase*

Rates are in M/l per sec.

| No. | Reaction | Solvent (Medium) | Unit of amount | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ N_2O_5 \rightarrow 2\ N_2O_4 + O_2$ | $N_2O_4$ | M/l | 0.2 | $k$ A | 15 | 1.6 | -5 | | * | ([1]) |
| | | | | | | 20 | 3.4 | -5 | 25 | | |
| | | $CH_3CHCl_2$ | " | " | " | 20 | 3.2 | -5 | | | " |
| | | | | | | 35 | 2.5 | -4 | 25 | | |
| | | $CHCl_3$ | " | " | " | 20 | 2.7 | -5 | | | |
| | | | | | | 25 | 5.5 | -5 | 25 | | " |
| | | $CH_2ClCH_2Cl$ | " | " | " | 20 | 2.4 | -5 | | | |
| | | | | | | 25 | 4.8 | -5 | 24 | | " |
| | | $CCl_4$ | " | 0.2 | " | 20 | 2.3 | -5 | | | |
| | | | | " | | 25 | 4.7 | -5 | 24 | | " |
| | | " | " | 5.3 | " | 45 | 6.7 | -4 | | | " |
| | | | | 2.3 | | " | 6.3 | -4 | | | |
| | | | | 1.4 | | " | 6.0 | -4 | | | |
| | | $C_2H_5Cl$ | " | 0.2 | " | 20 | 2.2 | -5 | | | " |
| | | | | | | 25 | 4.3 | -5 | 25 | | |
| | | $Br_2$ | " | " | " | 15 | 1.1 | -5 | | | " |
| | | | | | | 20 | 2.15 | -5 | 24 | | |

| No. | Reaction | Solvent (Medium) | Unit of amount | Amount of reactant | Defined mass-action law | Temperature | $k' = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ N_2O_5 \rightarrow 2\ N_2O_4 + O_2$ | $CH_3NO_2$ | M/l | 0.2 | $k\,A$ | 15 | 7.5 | −5 | | | (1) |
| | *(continued)* | | | | | 45 | 4.3 | −4 | 24.5 | | |
| | | S = 96 % $HNO_3$ aq | " | A/S = 0.043 | " | 45 | 2 | −5 | 28 (15 - 35°) | | |
| | | $CH_3CHClCH_2Cl$ | " | 2 | " | 20 | 2.0 | −6 | | | " |
| | | | | | | 35 | 2.0 | −5 | 27 | | |

## COMMENTS

Further data (2) (5). Interpretations (4) (3). See reaction in the gas phase 541.560.

## LITERATURE

(1) H. Eyring, F. Daniels, *ACS* 1930, 52, 1472, 1486. (2) C. N. Hinshelwood, The kinetics of chemical change, Oxford 1940. (3) R. H. Lueck, *ACS* 1922, 46, 757. (4) R. A. Ogg, Jr., *JCP* 1947, 15, 337. (5) F. O. Rice, D. Getz, *JPC* 1927, 31, 1572.

# DECOMPOSITION

## Nitramide

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NH_2NO_2 \rightarrow N_2O + H_2O$ | $H_2O$ | ~ 0.006 | | $kA = (k_o + \kappa[X] + k'A^-)A$ | | 25 | | | | | | * | (3) |
| | $(NH_2NO_2 = A)$ | | | | | | $k_o$ | 4.70 | -5 | | | | | |
| | $(NHNO_2^- = A^-)$ | | | | | | $k'$ | 3.68 | -2 | | | | | |
| | | | | | X = | $10^4$ [X]= | | | | | | | | |
| | | | | | $C_6H_5NH_2$ | 90.7 | $k$ | 4.99 | -4 | | | | | |
| | | | | | | | $\kappa$ | 4.8 | -2 | | | | | |
| | | | | | o-$ClC_6H_4NH_2$ | 90.1 | $k$ | 6.22 | -6 | | | | | |
| | | | | | | | $\kappa$ | 1.38 | -3 | | | | | |
| | | | | | m-$ClC_6H_4NH_2$ | 373 | $k$ | 3.38 | -6 | | | | | |
| | | | | | | | $\kappa$ | 7.70 | -2 | | | | | |
| | | | | | p-$ClC_6H_4NH_2$ | 17.3 | $k$ | 8.10 | -6 | | | | | |
| | | | | | | | $\kappa$ | 1.60 | -2 | | | | | |
| | | | | | $C_5H_5N$ | 26.8 | $k$ | 1.25 | -3 | | | | | |
| | | | | | | | $\kappa$ | 4.38 | -1 | | | | | |
| | | $H_2O$ | 0.1 | $OH^-$ | 0.01 | $kA$ | 25 | 1.15 | +4 | | | | | (7) |
| | | " | " | X = | [X] [HX] | $kA$ | | | | | | | | |
| | | | | $C_6H_5O^-$ | 0.01 0.01-0.1 | | 25 | 1.34 | +2 | | | | | (7) |
| | | | | 2, 4-$Cl_2C_6H_3O^-$ | 0.001 0.037 | | " | 8.9 | 0 | | | | | |
| | | | | o-$NO_2C_6H_4O^-$ | 0.001 0.0047 | | " | 1.83 | 0 | | | | | |
| | | | | 2, 4-$(NO_2)_2C_6H_3O^-$ | 0.05 Sat | | " | 1.32 | -2 | | | | | |
| | | | | $C_6H_5COO^-$ | 0.0 Sat | | " | 2.40 | -2 | | | | | |
| | | | | $CN^-$ | 0.0445 0.181 | | " | >1.1 | -1 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NH_2NO_2 \rightarrow N_2O + H_2O$ | | | | | $k_oA + k'A^-A + \kappa[X]A + k''A^-$ | | | | | | | | (7) |
| | $(NH_2NO_2 = A)$ | | | | | | 25 | | | | | | | |
| | $(NHNO_2^- = A^-)$ | | | | | | $k_o$ | 4.70 | -5 | | | | | |
| | | | | | | | $k'$ | 3.68 | -2 | | | | | |
| | *(continued)* | | | | | | $k''$ | 3.45 | -4 | | | | | |
| | | $H_2O$ | | HCl | 0.0057-0.057 | $k_oA$ | 15 | 1.45 | -5 | | | | | (1) (4) |
| | | | | $HClO_4$ | 0.0136 | | 25 | 4.68 | -5 | | | | | " |
| | | | | $C_6H_5SO_3H$ | 0.05 | | 35 | 1.50 | -4 | | | | | (1) |
| | | | | | | | 45 | 4.26 | -4 | 20.7 | 1.9 | 12 | | " |
| | | | | X = | $10^3[X]$ = | $kA = (k_o + \kappa[X])A$ | | | | | | | | |
| | | | | $(CH_3)_3CCOO^-$ | 8.5 - 17.4 | $\kappa$ | 15 | 8.22 | -1 | | | | | (1) |
| | | | | | 3.6 - 6.7 | | 25 | 2.30 | 0 | | | | | |
| | | | | | 27 - 36 | | 35 | 6.44 | 0 | 18.4 | 7.5 | 13 | | |
| | | | | $CH_3COO^-$ | 5 - 16 | $\kappa$ | 15 | 4.92 | -1 | | | | | (1) |
| | | | | | 6.4 - 8 | | 25 | 1.48 | 0 | | | | | |
| | | | | | 3.9 - 6.6 | | 35 | 4.28 | 0 | | | | | |
| | | | | | 2.7 - 8.2 | | 45 | 1.14 | +1 | 19.2 | 1.8 | 14 | | |
| | | | | $C_6H_5COO^-$ | 14 - 37.8 | $\kappa$ | 15 | 1.89 | -1 | | | | | (1) (4) |
| | | | | | 12.4 - 23.4 | | 25 | 5.5 | -1 | | | | | (1) |
| | | | | | 8.3 - 16 | | 35 | 1.57 | 0 | | | | | " |
| | | | | | | | 45 | 4.36 | 0 | 19.3 | 7.7 | 13 | | " |
| | | | | $HCOO^-$ | 34 - 47 | $\kappa$ | 15 | 8.2 | -2 | | | | | (1) (4) |
| | | | | | 27.4 - 50 | | 25 | 2.55 | -1 | | | | | (1) |
| | | | | | 26 - 35 | | 35 | 7.28 | -1 | | | | | " |
| | | | | | 7.6 - 21 | | 45 | 1.92 | 0 | 19.4 | 4.1 | 13 | | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NH_2NO_2 \rightarrow N_2O + H_2O$ | | | $OHC_6H_4COO^-$ | 47 - 95 | K | 15 | 2.08 | -2 | | | | | (1) (4) |
| | $(NH_2NO_2 = A)$ | | | | 89 - 137 | | 25 | 6.65 | -2 | | | | | (1) |
| | $(NHNO_2^- = A^-)$ | | | | 47 - 137 | | 35 | 2.05 | -1 | | | | | " |
| | | | | | 24.7 - 9.7 | | 45 | 5.45 | -1 | 20.1 | 3.7 | 13 | | " |
| | *(continued)* | | | $CH_2ClCOO^-$ | 65 - 176 | K | 25 | 4.65 | -2 | | | | | (1) |
| | | | | | 125 - 267 | | 35 | 1.33 | -1 | | | | | |
| | | | | | 26 - 176 | | 45 | 3.71 | -1 | 19.9 | 1.9 | 13 | | |
| | | | | $o\text{-}NO_2C_6H_4COO^-$ | 88 - 202 | K | 15 | 4.2 | -3 | | | | | (1) |
| | | | | | 77 - 239 | | 25 | 1.67 | -2 | | | | | |
| | | | | | 88 - 202 | | 35 | 5.18 | -2 | | | | | |
| | | | | | 77 - 180 | | 45 | 1.67 | -1 | 22.3 | 3.8 | 14 | | |
| | | | | $CHCl_2COO^-$ | 50 - 90 | K | 15 | 7.9 | -4 | | | | | (4) |
| | | | | | 247 - 419 | | 25 | 2.39 | -3 | | | | | (1) |
| | | | | | 196 - 424 | | 35 | 8.28 | -3 | | | | | " |
| | | | | | 184 - 510 | | 45 | 2.77 | -2 | 23.7 | 5.4 | 14 | | " |
| | | | | $COOHCOO^-$ | 14.5 | K | 15 | 0.00 | | | | | | (4) |
| | | | | $COO^-COO^-$ | 10.4 | " | " | 1.04 | -1 | | | | | |
| | | | | $COOHCH_2CH_2COO^-$ | 2.5 - 5.6 | K | 15 | 3.20 | -1 | | | | | (4) |
| | | | | $COO^-CH_2CH_2COO^-$ | 0.07 - 0.56 | " | " | 1.8 | 0 | | | | | |
| | | | | $COOH(CHOH)_2COO^-$ | 9 - 45 | K | 15 | 3.63 | -2 | | | | | (4) |
| | | | | $COO^-(CHOH)_2COO^-$ | 2.4 - 12 | " | " | 1.65 | -1 | | | | | |
| | | | | $H_2PO_4^-$ | 58 - 84 | K | 15 | 7.85 | -3 | | | | | (4) |
| | | | | $HPO_4^{--}$ | 0.002-0.01 | " | " | 8.6 | +1 | | | | | |
| | | | | $C_6H_5NH_2$ | 4.03 | k | 15 | 9.75 | -5 | | | | | (4) |
| | | | | | 6.44 | " | " | 1.47 | -4 | | | | | |
| | | | | | 10.7 | " | " | 2.28 | -4 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NH_2NO_2 \rightarrow N_2O + H_2O$ | $H_2O$ | | HCl | 0.001 - 0.03 | $kA$ | 25 | 4.70 | -5 | | | | | (6) |
| | | | | | 0.615 | | " | 5.40 | -5 | | | | | |
| | $(NH_2NO_2 = A)$ | | | | 1.45 | | " | 6.15 | -5 | | | | | |
| | $(NHNO_2^- = A^-)$ | | | HCl 0.01 + NaCl | 0.05 | | " | 4.66 | -5 | | | | | |
| | *(continued)* | | | | 0.48 | | " | 4.27 | -5 | | | | | |
| | | | | | 0.96 | | " | 3.83 | -5 | | | | | |
| | | | | | 2.38 | | " | 2.73 | -5 | | | | | |
| | | $H_2O + D_2O$ (atom %) | | | | $kA$ | | | | | | | | (5) |
| | | 0.0 | | | | | 28.8 | 4.83 | -5 | | | | | |
| | | 4.69 | | | | | " | 4.52 | -5 | | | | | |
| | | 28.10 | | | | | " | 3.30 | -5 | | | | | |
| | | 45.83 | | | | | " | 2.54 | -5 | | | | | |
| | | 77.91 | | | | | " | 1.09 | -5 | | | | | |
| | | 95.40 | | | | | " | 1.04 | -5 | | | | | |
| | | 96.67 | | | | | " | 9.62 | -6 | | | | | |
| | | (100.00) | | | | | " | (9.31) | -6 | | | | | |
| | | $C_6H_5OCH_3$ | ~ 0.1 | | $kA = (\kappa[X] + k''A^-)A =$ $k'A[X] = (\kappa + k''A^-/[X])A[X]$ | | | | | | | | * | (2) |
| | | | | X = | $10^3$ [X] = | | 25 | | | | | | | |
| | | | | $(C_2H_5)_3N$ | 0.9 - 4.1 | | $k'$ | 1.96 | -1 | | | | | |
| | | | | $(C_4H_9)_3N$ | 0.8 - 4.0 | | " | 3.91 | -1 | | | | | |
| | | | | $C_6H_5NH_2$ | 381 - 1023 | | $k'$ | 2.50 | -4 | | | | | |
| | | | | | | | $\kappa$ | 1.34 | -4 | | | | | |
| | | | | o-$ClC_6H_4NH_2$ | 202 - 650 | | $k'$ | 9.6 | -6 | | | | | |
| | | | | | | | $\kappa$ | 8.8 | -6 | | | | | |
| | | | | $C_6H_5NHCH_3$ | 270 - 730 | | $k'$ | 5.0 | -4 | | | | | |
| | | | | | | | $\kappa$ | 4.7 | -4 | | | | | |
| | | | | $C_5H_5N$ | 6 - 30 | | $k'$ | 3.21 | -2 | | | | | |
| | | | | | | | $\kappa$ | 3.12 | -2 | | | | | |

## COMMENTS

The first-order total rate of the decomposition (rate constant $k$) is representable by the sum of rates of a "spontaneous" first-order decomposition of A (rate constant $k_o$), a first-order decomposition of $A^-$, a second-order decomposition proportional to $A \times A^-$, and a base-catalyzed decomposition = $\kappa A[X]$ (X = base). Plots of log $\kappa$ against log $K$ (dissociation constant of the catalyzing base) are linear.

## LITERATURE

(1) E. C. Baughan, R. P. Bell, *PRS*[A] 1937, **158**, 464. (2) R. P. Bell, A. F. Trotman-Dickenson, *CSL* 1949, 1288. (3) R.P. Bell, G.L. Wilson, *TFS* 1950, **46**, 407. (4) J.N. Brönsted, K.Pedersen, *ZPC* 1924, **108**, 185. (5) V.K. LaMer, J.Greenspan, *TFS* 1937, **33**, 1266. (6) C. A. Marlies, V. K. LaMer, *ACS* 1935, **57**, 1812. (7) L. K. J. Tong, A. R. Olson, *ACS* 1941, **63**, 3406.



942151 O—51——32

# REDUCTIVE DECOMPOSITION

## OZONE

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\,O_3 \rightarrow 3\,O_2$ | $CCl_4$ | 0.00045-0.0021 | | | $k\,A$ | 54.7 | 1.8 | -5 | | | | * | (3) |
| | | | | | | | 71.0 | 1.23 | -4 | 26 | 5.82 | 12 | | |
| | | " | 0.0011-0.0034 | $Cl_2$ | 0.0002-0.011 | $k\,A^{3/2}[Cl_2]^{1/2}$ | (50) | (1.45) | -2 | | | | * | (3) |
| | | | | | | | 54.7 | 2.70 | -2 | | | | | |
| | | | | | | | 71.0 | 1.93 | -2 | 26.7 | 2.0 | 16 | | |
| .2 | $2\,O_3 \rightarrow 3\,O_2$ | $H_2O$ + $H_2SO_4$ 0.005 | 0.00177 | $H_2O_2$ | 0.00040 | $k\,A$ | 0 | 3.8 | -4 | | | | * | (6) |
| | | | 0.00150 | " | 0.000785 | " | " | 1.1 | -3 | | | | | " |
| | | | 0.00108 | " | 0.00169 | " | " | 2.0 | -3 | | | | | " |
| .3 | $2\,O_3 \rightarrow 3\,O_2$ | $H_2O$ | Sat | $OH^-$ | $(0.5\text{-}16) \times 10^{-13}$ | $k\,A\,[OH]^{1/2}$ | 0 | 1.41 | +2 | | | | * | (1) |
| | | | | | | | 27 | 1.38 | +3 | 9.9 | | | | |
| .4 | $2\,O_3 \rightarrow 3\,O_2$ | $H_2O$, pH < 1.6 | Sat | $Co^{++}$ = | $(6\text{-}36)10^{-5}$ | $k\,A\,[Co^{++}]$ | 0 | 3.7 | -1 | | | | * | (5) |
| | | | | | | | 17.4 | 1.15 | 0 | | $\Delta H_a = 9.0$ | | | |
| | | | | | | | 24.1 | 1.97 | 0 | | $\Delta S_a = -19$ | | | |
| | | | | | | | 30.6 | 2.93 | 0 | 9.6 | | | | |

## COMMENTS

(.1) In $CCl_4$, without $Cl_2$, some $COCl_2$ is formed, as one out of 18 molecules $O_3$ reacts with the solvent. Extrapolated to 50°C, the rate in $CCl_4$, without $Cl_2$, is about 30 times faster than in the gas phase. The solvent supplies activation equivalent to high-pressure gas reaction (see 541.660). In $CCl_4$, with $Cl_2$, $k$ tends to rise with the progress of the reaction. Extrapolated to 50°C, $k = 1.45 \times 10^{-2}$, is only about 50 % faster than in the gas phase, $9.50 \times 10^{-3}$. The rate law assumed in the presence of $Cl_2$ is the same as that obtaining in the gas phase ([3]); in the $CCl_4$ solution, in the presence of $Cl_2$, ([3]) find a rate law $kA[Cl_2]$ equally applicable. (.2) The reaction (*a*) $2\,O_3 \rightarrow 3\,O_2$ is accompanied by (*b*) $H_2O_2 + O_3 \rightarrow H_2O + O_2$, as evidenced by the concomitant decomposition of $H_2O_2$; in the three experiments tabulated, the ratio of decomposed $O_3$ to decomposed $H_2O_2$ is, respectively, (average) ~ 15, ~ 7, ~ 3. The ratio of the rates $(-d[O_3]/dt)/(-d[H_2O_2]/dt) = 1 + (5.2[O_3]/[H_2O_2])$. In terms of the interpretation of ([4]), rate (*a*) $= k_a\,[H_2O_2][O_3]$, and rate (*b*) $= k_b\,[H_2O_2][O_3]$; $k_a/k_b = 5.2[O_3]/[H_2O_2]$; $k_a + k_b = 1 + (5.2[O_3]/[H_2O_2])$. The interpretation assumes the mechanism $H_2O_2 + O_3 \rightarrow H_2O_3 + O_2$; $H_2O_3 + O_3 \rightarrow H_2O_2 + 2\,O_2$; $H_2O_3 + H_2O \rightarrow H_2O_2 + H_2O + O_2$. For chain mechanism, see ([7]). (.3) In solution in $H_2O$ ([1]), the $OH^-$ content is adjusted by $HClO_4$; $k$ is derived from spectrophotometry which gives the rate of disappearance of $O_3$. By iodimetry, i.e. by the total oxidizing power, the rate is independent of $[OH^-]$ and considerably below the rate determined by spectrophotometry. The hypothetical mechanism proposed is $O_3 + H_2O \rightarrow HO_3^+ + OH^-$ (slow); $HO_3^+ + OH^- \rightleftharpoons 2\,HO_2$ (maintained); $O_3 + HO_2 \rightarrow HO + 2\,O_2$ (slow); $HO + HO_2 \rightarrow O_2 + H_2O$. (.4) Iodometric determinations. In solutions acidified by $HClO_4$ or $H_2SO_4$, $k$ is independent of the acidity if pH < 1.6. The proportionality of the rate with $[Co^{++}]$ is approximate. The hypothetical mechanism, $Co^{++} + O_3 + H_2O \rightarrow CoOH^{++} + O_2 + HO$; $HO + O_3 \rightarrow HO_2 + O_2$; $HO_2 + CoOH^{++} \rightarrow Co^{++} + H_2O + O_2$, renders the observed rate law, if $CoOH^{++}/Co^{++}$ is constant.

## LITERATURE

(1) M.G. Alder, G.R. Hill, *ACS* 1950, **72**, 1880. (2) M. Bodenstein, E. Padelt, H.J. Schumacher, *ZPC*[B] 1929, **5**, 209. (3) E. J. Bowen, E. A. Moelwyn-Hughes, C. N. Hinshelwood, *PRS*[A] 1931, **134**, 211. (4) W. C. Bray, *ACS*, **1938**, 82. (5) G. R. Hill, *ACS* 1948, **70**, 1306. (6) V. Rothmund, A. Burgstaller, *MHC* 1917, **38**, 295. (7) J. Weiss, *TFS* 1935, **31**, 668.

# DECOMPOSITION
## with evolution of $N_2$
## from azo compounds

*Gas phase*

Amounts are in mm Hg.
Rates are in mm Hg per sec.
$k$ is in $sec^{-1}$.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .1 | $C_3H_7N{:}NC_3H_7 \rightarrow N_2 + C_6H_{14}$ | 4.6 – 0.26 | $k$ A | 250 | 4.60 | -4 | | | |
| | | | | 260 | 1.00 | -3 | | | |
| | | | | 270 | 1.92 | -3 | | | |
| | | | | 280 | 3.90 | -3 | | | |
| | | | | 290 | 7.7 | -3 | 40.9 | 5.6 | 13 |

## COMMENTS

Further decomposition $C_6H_{14} \rightarrow C_3H_6 + C_3H_8$ amounts to about 15 % of the total reaction; the first-order $k$ remains constant down to 0.26 mm Hg.

## LITERATURE

H. C. Ramsperger, *ACS* 1928, 50, 714.

# DECOMPOSITION

## CO group elimination from COOH

*Liquid phase*

Reaction type **RCOOH → ROH + CO**

Rate measured CO evolved.

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCOOH \rightarrow H_2O + CO$ | $H_2O + H_2SO_4$ 97.6 % | | $kA$ | 15 | 1.25 | -3 | | * | ([3]) |
| | | 94.5 | | | " | 3.80 | -4 | | | |
| | | 91.8 | | | " | 1.27 | -4 | | | |
| | | 98.9 | | | 25 | 1.23 | -2 | | | |
| | | 97.6 | | | " | 4.08 | -3 | 18.5 | | |
| | | 94.5 | | | " | 1.21 | -3 | 19.7 | | |
| | | 91.8 | | | " | 4.03 | -3 | 19.7 | | |
| | | 89.2 | | | " | 9.20 | -5 | | | |
| | | 85 | | | " | 2.88 | -5 | | | |
| | | 91.8 | | | 35 | 1.08 | -3 | | | |
| | | 88.9 | | | " | 4.15 | -4 | | | |
| | | 91.8 | | | 45 | 3.75 | -3 | | | |
| | | 88.9 | | | " | 1.19 | -3 | | | |
| | | $(CH_3CO)_2O$ | $C_5H_5N$ 0.035 | $kA$ | 50 | 1.7 | -4 | | * | |
| | | | 0.152 | | " | 5.7 | -4 | | | |
| | | | 0.281 | | " | 1.08 | -3 | | | |

| No. | Reaction | Solvent | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCOOH \rightarrow H_2O + CO$ *(continued)* | $(CH_3CO)_2O$ | Strychnine 0.0019 | $kA$ | 50 | 7.4 | -5 | | | |
| | | | 0.0075 | | " | 8.8 | -4 | | | |
| | | | 0.030 | | " | 4.2 | -3 | | | |
| .2 | $COOHCOOH \rightarrow H_2O + CO_2 + CO$ | See 562.446. | | | | | | | | |
| .3 | $COOHCHOHCH_2COOH \rightarrow CHOCH_2COOH + H_2O + CO$ | $H_2SO_4$ | | $kA$ | 20 | 1.27 | -4 | | | ([4]) |
| | | | | | 30 | 4.78 | -4 | | | |
| | | | | | 40 | 1.76 | -3 | 23.6 | | |
| | | " | X = | $kA$ | | | | | | |
| | | | | $\Delta \log (10^3 k)/\Delta X =$ | | | | | | |
| | | | $H_2O$ 0 - 1.25 | | 30 | -0.54 | | | | |
| | | | | | 40 | -0.61 | | | | |
| | | | $M_2SO_4$ 0 - 0.5 | | 40 | -1.27 | | | | |
| | | | $CH_3COOH$ 0 - 1.7 | | 40 | -0.60 | | | | |
| | | $H_2SO_4$ | | $kA$ | 20 | 1.85 | -4 | | | ([1a]) |
| | | | | | 25 | 3.96 | -4 | | | |
| | | | | | 30 | 7.86 | -4 | | | |
| | | | | | 35 | 1.55 | -3 | | | |
| | | " | $(NH_4)_2SO_4$ 0.25 | " | 20 | 5.67 | -5 | | | " |
| | | | | | 30 | 2.32 | -4 | | | |
| | | | | | 40 | 1.01 | -3 | | | |
| | | | " 0.50 | | 20 | 2.22 | -5 | | | " |
| | | | | | 30 | 1.04 | -4 | | | |
| | | | | | 40 | 4.60 | -4 | | | |

| No. | Reaction | Solvent | Addend | | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $COOHCHOHCH_2COOH \rightarrow CHOCH_2COOH + H_2O + CO$ *(continued)* | | $H_3PO_4$ | 0.25 | | 20 | 9.3 | -5 | | | ([1a]) |
| | | | | | | 30 | 4.28 | -4 | | | |
| | | | | | | 40 | 1.78 | -3 | | | |
| | | | " | 0.50 | | 20 | 5.93 | -5 | | | " |
| | | | | | | 30 | 2.72 | -4 | | | |
| | | | | | | 40 | 1.17 | -3 | | | |
| .4 | $(COOH)_2CH_2C(OH)COOH \rightarrow (CH_2COOH)_2CO + H_2O + CO$ | $H_2SO_4$ | $H_2O$ | 0.0 | $kA$ | 15 | 2.55 | -3 | | | ([5]) |
| | | | | 0.10 | | " | 3.58 | -3 | | | |
| | | | | 0.38 | | " | 1.75 | -3 | | | |
| | | | | 1.22 | | " | 2.07 | -4 | | | |
| | | | | 1.89 | | " | 7.2 | -5 | | | |
| | | | | 2.80 | | " | 2.1 | -5 | | | |
| | | | $H_2O$ | 0.0 | " | 25 | 7.3 | -3 | | | " |
| | | | | 0.14 | | " | 1.33 | -2 | | | |
| | | | | 0.25 | | " | 1.08 | -2 | | | |
| | | | | 1.04 | | " | 1.30 | -3 | | | |
| | | | | 2.03 | | " | 2.57 | -4 | | | |
| | | | | 3.07 | | " | 6.9 | -5 | | | |
| | | | $H_2O$ | 0.0 | " | 35 | 2.02 | -2 | | | " |
| | | | | 0.22 | | " | 3.53 | -2 | | | |
| | | | | 0.66 | | " | 1.15 | -2 | | | |
| | | | | 1.38 | | " | 2.62 | -3 | | | |
| | | | | 2.04 | | " | 9.9 | -4 | | | |
| | | | | 3.03 | | " | 2.9 | -4 | | | |

| No. | Reaction | Solvent | Addend | | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $(COOH)_2CH_2C(OH)COOH \rightarrow (CH_2COOH)_2CO + H_2O + CO$ *(continued)* | | $SO_3$ | 0.0 | $kA$ | 15 | 2.55 | -3 | | | ([5]) |
| | | | | 0.084 | | " | 1.13 | -3 | | | |
| | | | $SO_3$ | 0.00 | " | 25 | 7.3 | -3 | | | " |
| | | | | 0.084 | | " | 4.6 | -4 | | | |
| | | | | 0.15 | | " | 1.88 | -4 | | | |
| | | | $SO_3$ | 0.00 | " | 35 | 2.02 | -3 | | | " |
| | | | | 0.084 | | " | 1.57 | -3 | | | |
| .5 | $(C_6H_5)_3CCOOH \rightarrow (C_6H_5)_3COH + CO$ | $H_2SO_4 + H_2O$ 4 % | | | $kA$ | 12 | 1.02 | -3 | | | ([1]) |
| | | " | | | | 22 | 2.08 | -3 | | | |
| | | 5 | | | | 12 | 2.64 | -4 | | | |
| | | " | | | | 22 | 5.28 | -4 | 15.0 | | |
| | | 7 | | | | 5 | 1.10 | -4 | | | |
| | | " | | | | 22 | 3.07 | -4 | | | |
| | | $H_2SO_4$ | $Na_2SO_4$ | 12 % | $kA$ | 12 | 1.52 | -3 | | | |
| | | | | 14 | | 12 | 9.10 | -4 | | | |
| | | | | | | 22 | 2.85 | -3 | | | |
| | | | | 15 | - | 22 | 2.07 | -3 | | | |

## COMMENTS

(.1) In mixtures of concentrated $H_2SO_4$ with $CH_3COOH$ or with $(CH_3)_2CO$, the reaction proceeds at about the same rate as in $H_2SO_4$. Strong catalytic action of HCl (no numerical data). $Hg_2SO_4$, $CuSO_4$, $K_2SO_4$, $H_2SO_4$ have no appreciable effect on *k*. Older data of ([2]) are disregarded. In $(CH_3CO)_2O$, alkaloids (strychnine, brucine, nicotine, cocaine, quinine, papaverine, morphine) have an accelerating effect; data for alkaloids other than strychnine, in original ([3]). The relative effects of the alkaloids do not follow the order of their activities as bases. Contamination of the $(CH_3CO)_2CO$ solvent with $CH_3COOH$ lowers *k* in the presence of the alkaloids, but not with pyridine. The data are selected.

(.3) Data of ([4]) and ([1a]) in 100 % $H_2SO_4$ in not very satisfactory agreement. Effects of many other addends in original ([1a]). (.5) *k* averaged in the 20 - 60 % reaction range. Further data on effects of $K_2SO_4$, $CH_3COOH$, $C_6H_5OH$, $CH_3COCH_3$, etc., in original ([1]).

## LITERATURE

([1]) H.R.Dittmar, *JPC* 1929, **33**, 533.
([1a]) H.R.Dittmar, *ACS* 1930, **52**, 2746.
([2]) J.Meyer, *ZEC* 1909, **15**, 506.
([3]) E.R.Schierz, *ACS* 1923, **45**, 447.
([4]) E.L.Whitford, *ACS* 1925, **47**, 953.
([5]) E.O.Wiig, *ACS* 1930, **52**, 4729, 4737.

# DECOMPOSITION

## $CO_2$ evolution from COOH in aliphatic monocarboxylic acids

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

Reaction type **RCOOH → RH + $CO_2$**

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3COC(CH_3)_2COOH \rightarrow CH_3COCH(CH_3)_2 + CO_2$ | $H_2O + CH_3OH$ 25 % | 0.02 - 0.03 | HCl | 0.005 - 0.17 | *k*A | 25 | 7.1 | -5 | | * | ([5]) |
| | | 50 | 0.02 - 0.04 | " | 0.005 - 0.075 | " | " | 7.1 | -5 | | | |
| | | 75 | 0.02 - 0.06 | " | 0.001 - 0.05 | " | " | 6.5 | -5 | | | |
| | | $H_2O$ + dioxane 50 % | 0.04 - 0.06 | " | 0.003 - 0.01 | " | " | 8.0 | -5 | | | |
| | | $H_2O$ | | " | 0.01 - 0.18 | " | " | 6.8 | -5 | | | " |
| | | $H_2O$ | 0.02 | HCl + NaCl | | " | | | | | | |
| | | | | | 0.05 - 0.10 | | 25 | 6.9 | -5 | | * | ([3]) |
| | | | | | 0.2 - 0.5 | | " | 7.0 | -5 | | | |
| | | | | | 1.1 - 2.1 | | " | 7.2 | -5 | | | |
| | | | | | 0.1 - 0.2 | | 35 | 1.06 | -3 | | | |
| | | $H_2O$ | HCl + NaCl = | | 0.050 | " | | | | | | |
| | | | | HCl | 0.0272 | | 25 | 6.87 | -5 | | * | ([3]) |
| | | | | | 0.0169 | | " | 6.76 | -5 | | | |
| | | | | | 0.0053 | | " | 6.41 | -5 | | | |
| | | $H_2O$ | 0.015 - 0.018 | | | | | | | | | |
| | | | HCl 0.175 - 0.551; NaCl 0.040 | | | *k*A | 18.0 | 2.8 | -5 | | * | ([3]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CCC(CH_3)_2COOH \rightarrow CH_3COCH(CH_3)_2 + CO_2$ *(continued)* | $H_2O$ | | $CH_3COOH$ 0.3; | $CH_3COONa$ 0.3 | $kA$ | 18.0 | 1.7 | -6 | | * | (3) |
| | | | | 0.3 | 0.6 | " | " | 9.5 | -7 | | | |
| | | | | 0.5 | 0.5 | | " | 1.8 | -6 | | | |
| .2 | $NO_2CH_2COOH \rightarrow NO_2CH_3 + CO_2$ | $H_2O$ | 0.01 | HCl 0.01; | NaCl 0.09 | $kA$ | 20 | 9.41 | -4 | | * | (2) |
| | | | | 0.04 | 0.06 | | " | 5.75 | -4 | | | |
| | | | | 0.10 | 0 | | " | 3.07 | -4 | | | |
| | | | | 0.01 | 0 | | " | 8.85 | -4 | | | |
| | | " | " | pH 4.3 - 5.0 | | " | " | 1.21 | -3 | | | " |
| .3 | $CCl_3COOH \rightarrow CCl_3H + CO_2$ | $C_2H_5OH$ | 0.01 | X = | | $kA^{1/2}X^{1/2}$ | | | | | * | (4) |
| | | | | o-$ClC_6H_4NH_2$ | 0.1 | | 60 | 1.0 | -7 | | | |
| | | | | | " | | 70 | 4.1 | -7 | | | |
| | | | | m-$ClC_6H_4NH_2$ | 0.1 | | 60 | 2.0 | -7 | | | |
| | | | | | " | | 70 | 1.7 | -6 | | | |
| | | | | p-$ClC_6H_4NH_2$ | 0.1 | | 60 | 3.5 | -7 | | | |
| | | | | | " | | 70 | 1.2 | -6 | | | |
| | | | | $C_6H_5NH_2$ | 0.1 | | 60 | 7.8 | -7 | | | |
| | | | | | " | | 70 | 2.8 | -6 | | | |
| | | | | p-$CH_3C_6H_4NH_2$ | 0.1 | | 60 | 1.0 | -6 | | | |
| | | | | | " | | 70 | 3.8 | -6 | | | |
| | | | | α-$C_{10}H_9NHC_2H_5$ | 0.1 | | 60 | 3.2 | -7 | | | |
| | | | | | " | | 70 | 1.1 | -6 | | | |
| | | | | $C_6H_5NHCH_3$ | 0.1 | | 60 | 4.4 | -7 | | | |
| | | | | | " | | 70 | 1.6 | -6 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $CCl_3COOH \rightarrow CCl_3H + CO_2$ *(continued)* | | | $o$-$CH_3C_6H_4NHC_2H_5$ | 0.1 | | 60 | 4.8 | -7 | | | |
| | | | | | " | | 70 | 1.8 | -6 | | | |
| | | | | $p$-$CH_3C_6H_4NHCH_3$ | 0.1 | | 60 | 7.8 | -7 | | | |
| | | | | | " | | 70 | 3.3 | -6 | | | |
| | | | | $C_6H_5N(CH_3)_2$ | 0.1 | | 60 | 4.3 | -7 | | | |
| | | | | | " | | 70 | 1.6 | -6 | | | |
| | | | | $\alpha$-$C_{10}H_9N(CH_3)_2$ | 0.1 | | 60 | 2.4 | -7 | | | |
| | | | | | " | | 70 | 8.2 | -7 | | | |
| | | | | $CH_3C_5H_4N$ | 0:1 | | 60 | 3.8 | -7 | | | |
| | | | | | " | | 70 | 1.5 | +6 | | | |
| | | | | $C_5H_5N$ | 0.1 | | 60 | 4.7 | -7 | | | |
| | | | | | " | | 70 | 1.8 | -6 | | | |
| .4 | $CCl_3COO^- \rightarrow CCl_3^- + CO_2$ | $H_2O$ | 0.1 | | | $kA$ | 50 | 6.2 | -7 | | * | (4)(1) |
| | | | | | | | 60 | 3.5 | -6 | | | |
| | | | | | | | 70 | 1.7 | -5 | | | |
| | | | | | | | 80 | 7.9 | -5 | | | |
| | | | | | | | 90 | 3.2 | -4 | 36 | | |
| | | $C_2H_5OH$ | 0.005 - 0.1 | | | $kA$ | 50 | 1.3 | -5 | | | " |
| | | | | | | | 60 | 5.5 | -5 | | | |
| | | | | | | | 70 | 2.2 | -4 | 32 | | |
| | | $C_6H_5NH_2$ | 0.2 - 0.5 | | | $kA$ | 25 | 8.8 | -7 | | | " |
| | | | | | | | 35 | 4.0 | -6 | | | |
| | | | | | | | 45 | 1.6 | -5 | | | |
| | | | | | | | 55 | 5.8 | -5 | 26 | | |



942151 O—51——33

## COMMENTS

(.1) Good agreement of data of ([5]) and ([3]) at 25°C. The data refer to the rate of decomposition of the undissociated acid ([3]). At constant (HCl + NaCl), $k$ decreases slightly but distinctly with decreasing HCl acidity ([3]). In acetate buffers ([3]), the acid is partially dissociated; the data refer to the rate of decomposition of the undissociated acid. Data in glycolate buffers, in original ([3]).

(.2) Accelerated by KCl, $K_2SO_4$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, CsCl, $CO(NH_3)_6Cl$; slowed down by LiCl, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CuSO_4$, $CuCl_2$.

(.3) $k$ calculated from original data of $-1/2 \log k$. Proposed mechanism:

$CCl_3COOH + X^- \rightleftharpoons CCl_3COO^- + XH^+$; $CCl_3COO^- \rightarrow CCl_3^- + CO_2 (k_1)$; $CCl_3^- + XH^+ \rightarrow CCl_3H + X$ (fast); $k = 1/2\ k_1(K_A/K_{XH})$, where $K_A$, $K_{XH}$ = dissociation constants.

(.4) Reactants $CCl_3COONa$ and $CCl_3COOH \cdot H_2NC_6H_5$ in $H_2O$ and in $C_2H_5OH$; the latter only in $C_6H_5NH_2$; same values of $k$. Addition of HCl in equivalent amounts has no effect.

## LITERATURE

([1]) A.N.Kappanna, *ZPC* 1932, **158**, 355. ([2]) K.J.Pedersen, *TFS* 1927, **23**, 316. ([3]) K.J.Pedersen, *ACS* 1929, **51**, 2098; 1936, **58**, 240. ([4]) F.H.Verhoek, *ACS* 1934, **56**, 571; 1939, **61**, 186; 1945, **67**, 1062. ([5]) F.H.Westheimer, W.A.Jones, *ACS* 1941, **63**, 3283.

# DECOMPOSITION
## $CO_2$ evolution from COOH in aliphatic dicarboxylic acids

*Liquid phase*

Reaction type $R(COOH)_2 \rightarrow RHCOOH + CO_2$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | COOHCOOH (undissociated) → HCOOH + $CO_2$ (a); → $H_2O$ + CO + $CO_2$ (b) | $H_2O$ | ~ 0.4 | | | $(a + b) = kA$ | 100 | 1.2 | -7 | 42.6 | 1.2 | 18 | * | ([5a]) |
| | | | | | | | 140 | 3.0 | -5 | 39.8 | 3.2 | 16 | | |
| | | | | | | | 150 | 9.1 | -5 | 37.8 | 2.9 | 15 | | |
| | | | | | | | 160 | 2.5 | -4 | 34.8 | 9.2 | 13 | | |
| | | | | | | | 170 | 5.9 | -4 | 31.0 | 1.2 | 12 | | |
| | | dioxane | ~ 0.4 | | | $(a) = kA$ | 120 | 3.2 | -5 | | 7.5 | 11 | | " |
| | | | | | | | 140 | 2.0 | -4 | 29.9 | 7.7 | 11 | | |
| | | | | | | | 150 | 4.6 | -4 | 29.0 | 7.6 | 11 | | |
| .1.1 | COOHCOOH (undissociated) → $H_2O$ + CO + $CO_2$ | $H_2SO_4$ | | $H_2O$ | 0.60 % (a) | $kA$ | 70 | 3.02 | -4 | | | | * | ([11]) |
| | | | | | 0.80 " | | " | 1.70 | -4 | | | | | |
| | | | | | 1.20 " | | " | 8.18 | -5 | | | | | |
| | | | | | 1.50 % (m) | | " | 5.34 | -5 | | | | | |
| | | | | | 2.00 " | | " | 3.17 | -5 | | | | | |
| | | | | | 3.00 " | | " | 1.50 | -5 | | | | | |
| | | | | | 3.0 % (m) | " | 98 | 4.0 | -4 | | | | | " |
| | | | | | 6.0 % " | | " | 1.15 | -4 | | | | | |
| | | | | | 10.0 % " | | " | 3.7 | -5 | | | | | |
| | | | | | 20.0 % " | | " | 5.0 | -6 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1.2 | $C^{12}OOHC^{12}OOH \rightarrow H_2O + C^{12}O + C^{12}O_2$ (a) | $H_2SO_4$ | | | | $kA$ | 100 | | | | | | * | (10) |
| | $C^{13}OOHC^{12}OOH \rightarrow H_2O + C^{12}O + C^{13}O_2$ (b) | | | | | $k_b/k_c = 1.03$ | | | | | | | | |
| | $C^{13}OOHC^{12}OOH \rightarrow H_2O + C^{13}O + C^{12}O_2$ (c) | | | | | $k_a/(k_b + k_c) = 1.03$ | | | | | | | | |
| .2 | $CH_2(COOH)_2$ (A) $\rightarrow CH_3COOH + CO_2$ (a) | $H_2O$ | 0.005 - 0.05 | HCl | $(a + b) = k(A + A')$ | | | | | | | | * | (8) |
| | $CH_2(COOH)COO^-$ (A') $\rightarrow CH_3COO^- + CO_2$ (b) | | | (NaOH) | pH 0.42 | | 80 | 2.1 | -6 | | | | | |
| | | | | | " | | 90 | 7.2 | -6 | 31.0 | | | | |
| | | | | | 1.18 | | 80 | 2.1 | -6 | | | | | |
| | | | | | | | 90 | 7.0 | -6 | 30.7 | | | | |
| | [ See separate reactions a, b ] | | | | 1.98 | | 80 | 1.9 | -6 | | | | | |
| | (.2.1) (.2.2) | | | | | | 90 | 6.3 | -6 | 30.4 | | | | |
| | | | | | 2.40 | | 80 | 1.6 | -6 | | | | | |
| | | | | | | | 90 | 5.3 | -6 | 30.2 | | | | |
| | | | | | 3.28 | | 80 | 7.2 | -7 | | | | | |
| | | | | | | | 90 | 2.4 | -6 | 30.7 | | | | |
| | | | | | 4.02 | | 80 | 4.1 | -7 | | | | | |
| | | | | | | | 90 | 1.4 | -6 | 31.1 | | | | |
| .2.1 | $CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2$ | $H_2O$ | 0.005 - 0.05 | | | $kA$ | 80 | 2.1 | -6 | | | | * | (8) |
| | | | | | | | 90 | 7.1 | -6 | 30.8 | | | | |
| | | $H_2O$ | ~ 0.1 | | | $kA$ | 75.0 | 9.3 | -7 | | | | * | (2) |
| | | | | | | | 88.5 | 5.25 | -6 | | | | | |
| | | | | | | | 99.4 | 2.10 | -5 | | | | | |
| | | | | | | | 103.6 | 3.00 | -5 | | | | | |
| | | | | | | | 107.0 | 4.30 | -5 | | | | | |
| | | | | | | | 110.0 | 5.60 | -5 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2.2 | $CH_2(COOH)COO^- \rightarrow CH_3COO^- + CO_2$ | $H_2O$ | 0.5 | | | $kA$ | 76.3 | 3.38 | −7 | | | | * | (7) (8) |
| | | | | | | | 100 | 5.00 | −6 | | | | | |
| | | | | | | | 120 | 3.05 | −5 | 28.1 | 1.48 | 11 | | |
| .2.3 | $COOHC^{12}H_2C^{12}OOH \rightarrow CH_3COOH + C^{12}O_2$ (a) | fused | | | | $kA$ | | | | | | | * | (12) |
| | $COOHC^{12}H_2C^{14}OOH \rightarrow CH_3COOH + C^{14}O_2$ (b) | | | | | $k_a/k_b = 1.12$ | | | | | | | | |
| .3 | $COOHC^{12}HBrC^{12}OOH \rightarrow CH_2BrCOOH + C^{12}O_2$ | fused | | | | $kA$ | | | | | | | * | (12) |
| | | | | | | $k_a/k_b = 1.43$ | | | | | | | | |
| .4 | $CBR_2(COOH) \rightarrow CHBr_2COOH + CO_2$ | $H_2O$ | 0.009–0.02 | KCl 1 + HCl | 0.0 | $kA$ | 25.0 | 1.26 | −4 | | | | * | (11) |
| | | | | | 0.08 | | " | 1.62 | −4 | | | | | |
| | | | | | 0.10 | | " | 1.74 | −4 | | | | | |
| | | | | | 0.25 | | " | 1.76 | −4 | | | | | |
| | | | | | 0.50 | | " | 1.55 | −4 | | | | | |
| | | | | | 0.75 | | " | 1.24 | −4 | | | | | |
| | | | | | 1.0 | | " | 1.08 | −4 | | | | | |
| .4.1 | $CBr_2(COOH)COO^- \rightarrow CHBrCOO^- + CO_2$ | $H_2O$ | 0.009–0.2 | KCl 1 + HCl | 0.0 – 1.0 | $kA$ | 25.0 | 2.18 | −4 | 25.0 (25–35°) | | | * | (11) |
| | | | | buffers, pH 0.9–3.7 | | " | " | 2.18 | −4 | | | | | " |
| | | | | | 4.1–4.7 | | " | 1.8 | −4 | | | | | |
| .5 | $CH_3CH(COOH)_2 \rightarrow C_2H_5COOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.6 | 1.66 | −5 | | | | | (2) |
| .6 | $COOHC{:}CCOOH \rightarrow HC{:}CCOOH + CO_2$ | $H_2O$ | 0.027 | | | $kA$ | 100 | 1.3 | −6 | | | | | (6) |
| | | | | | | | 131.5 | 1.2 | −5 | | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6.1 | $COOH{:}CCOOC_2H_5 \rightarrow HC{:}CCOOC_2H_5 + CO_2$ | $H_2O$ | 0.09 | | | $kA$ | 100.5 | 1.1 | -4 | | | | | (6) |
| | | $C_6H_5CH_3$ | 0.07 | | | " | " | 1.8 | -5 | | | | | |
| .6.2 | $COOHC{:}CCOOK \rightarrow HC{:}CCOOK + CO_2$ | $H_2O$ | 0.06 | | | $kA$ | 60 | 2.7 | -5 | | | | * | (6) |
| .7 | $C_2H_5CH(COOH)_2 \rightarrow C_3H_7COOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.4 | 1.41 | -5 | | | | | (2) |
| .8 | $(CH_3)_2C(COOH)_2 \rightarrow (CH_3)_2CHCOOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.4 | 8.25 | -6 | | | | | (2) |
| .9 | $(CH_3)(C_2H_5)C(COOH)_2 \rightarrow (CH_3)(C_2H_5)CHCOOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.2 | 8.95 | -6 | | | | | (2) |
| .10 | $CH_2{:}CHCH_2CH(COOH)_2 \rightarrow CH_2{:}CHCH_2CH_2COOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.5 | 3.68 | -5 | | | | | (2) |
| .11 | $(C_2H_5)_2C(COOH)_2 \rightarrow (C_2H_5)_2CHCOOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.6 | 7.80 | -6 | | | | | (2) |
| .12 | $(C_3H_7)_2C(COOH)_2 \rightarrow (C_3H_7)_2CHCOOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.5 | 1.36 | -5 | | | | | (2) |
| .13 | $(CH_2CH{:}CH_2)_2C(COOH)_2 \rightarrow (CH_2CH{:}CH_2)_2CHCOOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.5 | 1.8 | -5 | | | | | (2) |
| | **Aryl - substituted aliphatic dicarboxylic acids** | | | | | | | | | | | | | |
| .14 | $C_6H_5CH(COOH)_2 \rightarrow C_6H_5CH_2COOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 66 | 9.53 | -5 | | | | | (2) |
| | | | | | | | 88.5 | 7.28 | -4 | | | | | |
| | | A (pure liquid) | | | | $kA$ | 125 | 1.53 | -4 | | | | * | (5) |
| | | | | | | | 135 | 4.05 | -4 | 11.3 | | | | |
| | | $C_{17}H_{33}COOH$ | 0.1-0.3 | | | " | 125 | 1.61 | -4 | | | | | (5) |
| | | | | | | | 135 | 3.79 | -4 | 10.4 | | | | |

| No. | Reaction | Solvent (Medium) | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .14 | $C_6H_5CH(COOH)_2 \rightarrow C_6H_5CH_2COOH + CO_2$ *(continued)* | $C_{15}H_{33}COOH$ | 0.1-0.3 | | | $kA$ | 135 | 3.72 | -4 | | | | | (5) |
| | | $o$-$NO_2C_6H_4Cl$ | " | | | " | " | 4.62 | -4 | | | | | " |
| | | $m$-$NO_2C_6H_4Cl$ | " | | | " | " | 5.08 | -4 | | | | | " |
| | | $p$-$NO_2C_6H_4Cl$ | " | | | " | " | 4.44 | -4 | | | | | " |
| | | $C_6H_5N(CH_3)_2$ | " | | | " | " | 2.80 | -3 | | | | | " |
| .15 | $C_6H_5CH_2CH(COOH)_2 \rightarrow C_6H_5CH_2CH_2COOH + CO_2$ | $H_2O$ | ~ 0.1 | | | $kA$ | 99.5 | 5.5 | -5 | | | | | (2) |
| | **Diazomalonates** | | | | | | | | | | | | | |
| .16 | (a) $N_2C(COO^-)_2$ (A) + $H^+$ + $H_2O$ <br> (b) $N_2C(COOH)COO^-$ (A') + $H_2O$ <br> $\rightarrow N_2 + CH_2OHCOO^- + CO_2$ | $H_2O$ | A + A' = 0.006 | $HClO_4$ | (a + b) = k(A + A') <br> 0.01 | | 25 | 3.30 | -4 | | | | * | (9) |
| | | | | | 0.04 | | " | 7.70 | -4 | | | | | |
| | | | | | 0.10 | | " | 1.25 | -3 | | | | | |
| | | | | | 0.20 | | " | 1.53 | -3 | | | | | |
| | | | | | (a) = k A [$H^+$] | | | | | | | | * | (9) |
| | | " | " | $HClO_4$ | 0.01-0.20 | | 25 | 3.17 | -2 | | | | | |
| .17 | (a) $N_2C(COOC_2H_5)COO^-$ (A) + $H^+$ + $H_2O$ <br> (b) $N_2C(COOC_2H_5)COOH$ (A') + $H_2O$ <br> $\rightarrow N_2 + CH_2OHCOOC_2H_5 + CO_2$ | $H_2O$ | A + A' = 0.006 | $HClO_4$ | (a + b) = k(A + A') <br> 0.01 | | 25 | 4.0 | -4 | | | | * | (9) |
| | | | | | 0.04 | | " | 7.9 | -4 | | | | | |
| | | | | | 0.10 | | " | 8.4 | -4 | | | | | |
| | | | | | 0.20 | | " | 8.8 | -4 | | | | | |
| | | | | | 0.50 | | " | 1.05 | -3 | | | | | |
| | | | | | (a) = k A [$H^+$] | | | | | | | | | |
| | | | " | $HClO_4$ | 0.01-0.50 | | 25 | 1.53 | -1 | | | | * | (9) |

(.1) Thermal decomposition in pressure bomb. In $H_2O$, 37 % of the decomposition follow reaction (*a*), 63% reaction (*b*); in dioxane, only reaction (*a*) occurs.

(.1.1) Decomposition through dehydration by concentrated $H_2SO_4$. Selected points. ([a]) means % based on 100 g $H_2SO_4$, ([m]) is % based on 100 g mixture. Rate constant *k* remains constant only as long as the amount of $H_2O$ produced remains small as compared with that present initially. Addition of 0.1% $H_2O$ to 100.0% $H_2SO_4$ lowers the rate 17 fold. Addition of 1% $SO_3$ makes the reaction too rapid to measure at 0°C. (.1.2) The ratio $k_a/(k_b + k_c)$ involves the relative rates of rupture of the $C^{12} - C^{12}$ and the $C^{12} - C^{13}$ bond. (.2) (.2.1) (.2.2) Reaction (.2.2) is faster than (.2.1). For (.2.2), data of ([7]) are obtained with a solution of $CH_2(COOH)COONa$. For (.2.1) (*a*), data of ([8]) derived from the overall reaction (.2) (*a* + *b*) minus reaction (.2.2) (*b*), are in line with the experimental data of ([2]) on solutions of $CH_2(COOH)_2$ which should be partly ionized. (.2.3) (.3) The ratio $k_a/k_b$ involves the relative rates of rupture of $C^{12} - C^{12}$ and $C^{12} - C^{14}$ bonds. See further ([3]). (.4) (.4.1) Reaction, (.4) actually proceeds through decomposition of the $CBr_2(COOH)COO^-$ ion, i.e. through reaction (.4.1). The rate constant for reaction (.4.1) is won from *k* of reaction (.4) by division by $\alpha = [CBr_2(COOH)COO^-] / ([CBr_2(COOH)COO^-] + [CBr_2(COOH)_2])$, with $\alpha$ from the dissociation constant $[CBr_2(COOH)COO^-]\ [H^+]/[CBr_2(COOH)_2]$.

(.6.2) First-order only at 60°C; at 80° and 98.5°C, further reactions $HC{:}CCOOK + H_2O \longrightarrow KHCO_3 + C_2H_2$; $2\ KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$; $COOHC{:}CCOOK + KHCO_3(K_2CO_3) \longrightarrow COOKC{:}CCOOK$, which is more stable. (.14) *k* calculated from original half-time data ([5]).

(.16) (.17) Reactants are $N_2C(COOK)_2$ in reaction (.16) and $N_2C(COOC_2H_5)COOK$ in reaction (.17). The total reactions (*a* + *b*) are interpreted by the equilibria $A' \rightleftharpoons A + H^+$ (equilibrium constant *K*) and the rate constants are related by $k_{a+b}\ (A + A') = k_a\ A[H^+]$, hence $k_{a+b} = k_a[H^+]K/(K + [H^+])$; the rate constant $k_a$ and the equilibrium constant *K* are obtained from linear plots of $k_{a+b}/[H^+]$ against $k_{a+b}$. For (.16) *K*=0.066, and for (.17), *K*=0.0059. $CH_3COOH$ added to $HClO_4$ has no measurable effect, but in acetate buffers pH ~ 5, there is base catalysis by the $CH_3COO^-$ ion, maximum at $CH_3COOH$ = 0.06. At this concentration of $CH_3COOH$, $k_{a+b}$ increases linearly with $[CH_3COO^-]$.

## LITERATURE

(1) A. L. Bernouilli, W. Wege, *HCA* 1919, **2**, 511. (2) A. L. Bernouilli, W. Wege, *HCA* 1919, **2**, 515. (3) J. Bigeleisen, *JCP* 1949, **17**, 425. (4) G. Bredig, D. M. Lichty, *ZEC* 1906, **12**, 459. (5) R. E. Burk, W. Daus, *JPC* 1931, **35**, 1461. (5a) A. Dinglinger, E. Schroer, *ZPC*[A] 1937, **179**, 401. (6) M.S. Dudkin, ZhOKh 1950, **20**, 1729. (7) R. A. Fairclough, *CSL* 1938, 1186. (8) G. A. Hall, Jr., *ACS* 1949, **71**, 2691. (9) C. V. King, P. Kulka, A. Mebane, *ACS*, 1950, **72**, 1906. (10) J.G. Lindsay, D.E. McElcheran, H.G. Thode, *JCP* 1949, **17**, 589. (11) J. Muus, *JPC* 1935, **39**, 343. (12) P. E. Yankwich, M. Calvin, *JCP* 1949, **17**, 109.

# DECOMPOSITION
## with evolution of $CO_2$ from aromatic carboxylic acids

Reaction type $\left.\begin{matrix}ArCOOH\\ ArCOO^-\end{matrix}\right\} \rightarrow CO_2 + \left\{\begin{matrix}ArH\\ Ar^-\end{matrix}\right.$

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | 2, 4, 6-$(NO_2)_3C_6H_2COO^-$ | $C_2H_5OH$ | $10^3A$ = 4.82 | | | $k\,A$ | 35 | 7.7 | -5 | | | | * | ([2]) |
| | | | 9.96 | | | | " | 7.0 | -5 | | | | | |
| | | | 10.18 | | | | " | 7.4 | -5 | | | | | |
| | | | 19.88 | | | | " | 6.2 | -5 | | | | | |
| | | | 4.82 | | | " | 45 | 3.1 | -4 | | | | | |
| | | | 9.96 | | | | " | 2.8 | -4 | | | | | |
| | | | 10.18 | | | | " | 3.0 | -4 | | | | | |
| | | | 19.88 | | | | " | 2.4 | -4 | 27.0 | | | | |
| .2 | 2, 4, 6-$(NO_2)_3C_6H_2COOH$ | $C_2H_5OH$ | $10^3A$ = 4.20 | $X = C_6H_5NH_2$ | 0.001 - 0.1 | $k\,A^{1/2}\,X^{1/2}$ | 35 | 3.5 | -5 | | | | * | ([2]) |
| | | | | | | | 45 | 1.3 | -4 | | | | | |
| | | | | o-$ClC_6H_4NH_2$ | " | " | 35 | 3.4 | -6 | | | | | |
| | | | | | | | 45 | 1.3 | -5 | | | | | |
| | | | | m-$ClC_6H_4NH_2$ | " | " | 35 | 9.8 | -6 | | | | | |
| | | | | | | | 45 | 3.7 | -5 | | | | | |
| | | | | p-$ClC_6H_4NH_2$ | " | " | 35 | 1.5 | -5 | | | | | |
| | | | | | | | 45 | 5.6 | -5 | | | | | |
| | | | | p-$CH_3C_6H_4NH_2$ | " | " | 35 | 4.7 | -5 | | | | | |
| | | | | | | | 45 | 1.9 | -4 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | 2, 4, 6-$(NO_2)_3C_6H_2COOH$ *(continued)* | $C_2H_5OH$ | $10^3A = 4.20$ | $C_6H_5N(CH_3)_2$ | 0.001 - 0.1 | $k A^{1/2}x^{1/2}$ | 35 | 1.2 | -5 | | | | | |
| | | | | | | | 45 | 4.6 | -5 | | | | | |
| .3 | 2, 4, 6-$(NO_2)_3C_6H_2COOH$ | $H_2O$ | | | | $k A$ | 60 | 2.3 | -6 | | | | * | ([1]) |
| | | | | | | | 70 | 1.1 | -5 | | | | | |
| | | $H_2O$ | | | $1/2\ kK[(1 + 4A/K)^{1/2} - 1]$ | | 60 | 2.3 | -6 | | | | | " |
| | | | | | | | 70 | 1.1 | -6 | 36 | 9 | 18 | | |
| | | $H_2O$ + dioxane 20 % | | | | " | 60 | 1.5 | -5 | | | | | " |
| | | | | | | | 70 | 7.0 | -5 | | | | | |
| | | | 40 % | | | " | 60 | 1.4 | -4 | | | | | " |
| | | | | | | | 70 | 5.8 | -4 | | | | | |
| | | | 60 % | | | " | 60 | 9.2 | -4 | | | | | " |
| | | | | | | | 70 | 3.0 | -3 | | | | | |
| | | | 80 % | | | | 60 | 5.2 | -3 | | | | | |
| | | | | | | | 70 | 1.5 | -2 | 23 | 1 | 14 | | |

## COMMENTS

(.1) The data refer to the Li salt; close values for the Na salt. (.2) The order, 1/2 in A and 1/2 in X, indicates clearly that the rate of the reaction is governed by the rate of decomposition of the anion of the corresponding anilinium salt. (.3) First order in the acid holds only in $H_2O$ and, approximately, in low-dioxane solvents. At greater dioxane concentrations, the rate $-dA/dt$ follows the order given as definition of $k$, involving the dissociation constant $K$ of the acid in the given medium and indicating the decomposition of the anion as the rate-determining step. The empirical order of the reaction with respect to A falls from 1 in $H_2O$ to about 1/2 in 90 % dioxane. In 20 %, 40 %, 60 %, 80 % dioxane, $K$ = 0.3, 0.031, 0.002, 0.0000047. The observed rates of decomposition at an initial [A] = 0.008, are:

| *Solvent* | | $H_2O$ | $H_2O$ + dioxane 20 % | 40 % | 60 % | 80 % | 89 % |
|---|---|---|---|---|---|---|---|
| $-10^8(dA/dt)$ | 60°C | 1.8 | 13 | 90 | 274 | 98 | 9.5 |
| | 70°C | 8.9 | 58 | 346 | 948 | 276 | 24.4 |

i.e. passing through a maximum.

## LITERATURE

(1) D. Trivich, F. H. Verhoek, *JCS* 1943, 65, 1919.

(2) F. H. Verhoek, *JCS* 1939, 61, 186.

# DECOMPOSITION

## Evolution of $N_2$ from diazonium halides

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $ArN_2Cl \rightarrow ArCl + N_2$

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5N_2Cl$ | $H_2O$ | 0.1 | HCl | pH 1.6 - 1.8 | $k$ A | 5 | 1.5 | -6 | | | | * |
| | | | | | | | 25 | 4.10 | -5 | | | | |
| | | | | | | | 35.2 | 2.00 | -4 | | | | |
| | | | | | | | 50 | 1.40 | -3 | 27.2 | 3.6 | 15 | |
| | | | 0.1 | HCl | 0.1 | " | 35.2 | 2.00 | -4 | | | | |
| | | | | | 5.0 | | " | 2.35 | -4 | | | | |
| | | | | | 10.0 | | " | 2.41 | -4 | | | | |
| | | | | | 12.0 | | " | 2.26 | -4 | | | | |
| .2 | o-$CH_3C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | 35.2 | 9.58 | -4 | 26.2 | 3.5 | 15 | |
| .3 | m-$CH_3C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (10 - 35°) | | | 25.7 | 1.3 | 15 | |
| .4 | p-$CH_3C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (25 - 55°) | | | 27.5 | 7.1 | 14 | |
| .5 | m-$CH_3OC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (15 - 30°) | | | 24.6 | 2.1 | 14 | |
| .6 | p-$CH_3OC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (60 - 80°) | | | 32.5 | 3.9 | 15 | |
| .7 | o-$COOHC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (25 - 40°) | | | 29.4 | 2.6 | 16 | |
| .8 | m-$COOHC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (30 - 40°) | | | 27.1 | 1.7 | 15 | |
| .9 | p-$COOHC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (40 - 55°) | | | 27.7 | 1.1 | 15 | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of Addend | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .10 | o-$OHC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (50 - 60°) | | | 30.4 | 7 | 15 | |
| .11 | m-$OHC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (20 - 30°) | | | 26.0 | 5.5 | 15 | |
| .12 | p-$OHC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (50 - 60°) | | | 23.6 | 3.2 | 11 | |
| .13 | o-$NO_2C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (60 - 80°) | | | 26.5 | 5.9 | 11 | |
| .14 | m-$NO_2C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (60 - 80°) | | | 33.2 | 7.0 | 16 | |
| .15 | p-$NO_2C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (60 - 80°) | | | 29.8 | 1.2 | 15 | |
| .16 | o-$C_6H_5C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (20 - 45°) | | | 25.5 | 3.2 | 14 | |
| .17 | m-$C_6H_5C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (15 - 35°) | | | 22.8 | 5.3 | 12 | |
| .18 | p-$C_6H_5C_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (30 - 55°) | | | 27.6 | 3.5 | 14 | |
| .19 | o-$SO_3HC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (40 - 50°) | | | 30.3 | 7.9 | 16 | |
| .20 | m-$SO_3HC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (40 - 50°) | | | 28.0 | 2.9 | 15 | |
| .21 | p-$SO_3HC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (40 - 55°) | | | 27.4 | 2.9 | 14 | |
| .22 | o-$ClC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (60 - 90°) | | | 30.8 | 2.6 | 14 | |
| .23 | m-$ClC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (40 - 55°) | | | 30.2 | 2.1 | 16 | |
| .24 | p-$ClC_6H_4N_2Cl$ | $H_2O$ | 0.1 | HCl | 0.02 | $k$ A | (60 - 80°) | | | 31.6 | 1.1 | 16 | |

## COMMENTS

Measurements of amount of $N_2$ evolved. (.1) First order over 96 % of the conversion. In dilute solution, the reaction is $A \rightarrow N_2 + C_6H_5Cl \xrightarrow{H_2O} N_2 + HCl + C_6H_5OH$, with a 95 % yield of $C_6H_5OH$ (at $H_2O/A = 1280$); in concentrated solution, the yield of $C_6H_5OH$ falls to 24 % (at $H_2O/A = 2.4$), and the products are $C_6H_5Cl$, $C_6H_6$, and $C_6H_5C_6H_5$. The effect of acid concentration is very slight.

## LITERATURE

M. L. Crossley, R. H. Kienle, C. H. Benbrook, *JACS* 1940, 62, 1400.



942151 O—51——34

# PYROLYSIS
## Aliphatic hydrocarbons

*Gas phase*

All rates are in "unit of amount" per sec.

Comments, Mechanism, Literature, at the end of the table.

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Amount of addend | Rate measured | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6$ | p | mm Hg | 13 - 385 | | - | +p | kA | 735 | 1.2 | -7 | | | | * | ([17]) |
| | | | | | | | | | 800 | 6.0 | -7 | | | | | " |
| | | | | | | | | | 976 | 1.3 | -6 | | | | | " |
| | | | | | | | | | 1008 | 4.3 | -6 | | | | | " |
| | | | | | | | | | 1061 | 3.2 | -5 | | | | | " |
| | | | | | | | | | 1113 | 1.9 | -4 | 79 | 1.0 | 12 | | " |
| | | " | " | 100 | - | - | " | " | 850 | 2.8 | -6 | | | | * | ([13]) |
| | | | | 200 | - | - | | | " | 3.4 | -6 | | | | | " |
| .1.1 | $CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6$ | " | " | 100 | NO | 0 | " | " | 850 | 2.8 | -6 | | | | * | ([13]) |
| | | | | " | | 6.1 | | | " | 1.5 | -6 | | | | | " |
| | | | | " | | 10 | | | " | 2.0 | -6 | | | | | " |
| | | | | " | | 23 | | | " | 3.8 | -6 | | | | | " |
| | | | | 200 | " | 0 | " | " | " | 3.4 | -6 | | | | * | " |
| | | | | " | | 6.5 | | | " | 2.1 | -6 | | | | | " |
| | | | | " | | 14.5 | | | " | 2.8 | -6 | | | | | " |
| | | | | " | | 26 | | | " | 4.1 | -6 | | | | | " |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Amount of addend | Rate measured | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6$ | flow anal | mm Hg | 760 | | | −A | $k$ A | | | | | | | * | ([10]) |
| | | | | | | $100(A_o - A)/A_o$ | | | | | | | | | | " |
| | | | | | | 1.27 | | | 1007 | 4.4 | −2 | | | | | " |
| | [See Supplementary Table] | | | | | 10.54 | | | " | 7.4 | −2 | | | | | " |
| | | | | | | 1.27 | | | 1033 | 5.8 | −2 | | | | | " |
| | | | | | | 10.88 | | | " | 1.07 | −1 | | | | | " |
| | | | | | | 16.91 | | | " | 1.22 | −1 | | | | | " |
| | | | | | | 2.29 | | | 1053 | 1.25 | −1 | | | | | " |
| | | | | | | 9.66 | | | " | 1.77 | −1 | | | | | " |
| | | | | | | 3.96 | | | 1075 | 2.50 | −1 | | | | | " |
| .3 | $C_2H_6 \rightarrow C_2H_4 + H_2$ | p, anal | mm Hg | | | | +p | $k$ A | 551 | 2.8 | −5 | | | (+p) | ([32]) | ([18]) |
| | | | | 100 − 1500 | | −A; | +M | | 565 | 6.4 | −5 | | | (+M) | | ([43]) |
| | | | | | | | −A | | 572 | 8.9 | −5 | | | (−A) | ([38]) | ([19]) |
| | | | | | | | " | | 580 | 1.2 | −4 | | | | | |
| | | | | | | | +p | | 583 | 1.7 | −4 | | | | | |
| | | | | | | | −A | | 595 | 2.8 | −4 | | | | | |
| | | | | | | | " | | 600 | [7.9] | −4 | | | | | |
| | | | | | | | " | | 607 | 4.6 | −4 | | | | | |
| | | | | | − | +p; | −A | | 614 | 7.6 | −4 | | | | | |
| | | | | | | | −A | | 625 | 1.0 | −3 | | | | | |
| | | | | | − | +p; | −A | | 638 | 1.9 | −3 | | | | | |
| | | | | | | | +p | | 663 | 7.4 | −3 | 70 | 1 | 15 | * | |
| | | | | | | | −A | | 668 | [1.4] | −2 | | | | | |
| | | | | | | | " | | 675 | [2.9] | −2 | | | | | |
| | | | | | | | " | | 700 | [3.6] | −2 | | | | | |

| No. | Reaction | Medium | Unit of amount | Amount of reactant | Addend | Amount of addend | Rate measured | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $C_2H_6 \rightarrow C_2H_4 + H_2$ | p | mm Hg | 150 | NO | 0 | +p | $k$ A | 620 | 5.9 | -4 | | | | | (35) |
| | | | | | | 1.25 | | | " | 1.9 | -4 | | | | | " |
| | | | | | | 18.5 | | | " | 4.7 | -5 | | | | | " |
| | | | | | | 35.5 | | | " | 5.0 | -5 | | | | | " |
| | | | | | | 50.5 | | | " | 4.8 | -5 | 74.5 | | | | " |
| | | anal | 300 - 550 | | NO | 1% | -A | $k$ A | 565 | 1.3 | -5 | | | | | (38) |
| | | | | | | " | | | 607 | 1.2 | -4 | | | | | " |
| | | | | | | " | | | 640 | 7.7 | -4 | 77.3 | | | | " |
| .5 | $C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow CH_4, C_{>4}$ | anal | M/l | A = 0.025 | | - | +L | $k$ AB | 590 | 1.4 | -2 | See Supplementary Table | | | * | (41) |
| | (A) (B) (C) (R) | | | | | | +R | $k B^2$ | " | 3.3 | -2 | | | | | " |
| .5.1 | $C_2H_6 + C_2H_4 + H_2 \rightarrow CH_4, C_{>4}$ | " | " | $A \rightleftarrows B + C$ | | - | +L | $k B(A + B + C)$ | | | | | | | * | (41) |
| | | | A + B = 0.025 | | | | | | 550 | 1.7 | -3 | | | | | " |
| | | | | | | | | | 590 | 5.6 | -3 | | | | | " |
| | | | | | | | | | 620 | 1.2 | -2 | 41 | | | | " |
| | | | " | | | | +R | $k B^2$ | 550 | 8.1 | -3 | | | | * | " |
| | | | | | | | | | 590 | 2.1 | -2 | | | | | " |
| | | | | | | | | | 620 | 3.9 | -2 | 35 | | | | " |
| | | | " | 0.01 - 0.04 | | | +(L + R) | $k$ AB | 550 | 2.3 | -3 | | | | (41) | (39) |
| | | | | | | | | | 590 | 1.1 | -2 | | | | | " |
| | | | | | | | | | 620 | 3.1 | -2 | 55 | | | * | " |
| .6 | $C_3H_8 \rightarrow C_3H_6 + H_2$ (a); $C_3H_8 \rightarrow C_2H_4 + CH_4$ (b) | p | mm Hg | ∞ | - | - | +p | $k$ A | 551 | 1.84 | -4 | | | | | (37) |
| | | | | | | | | | 572 | 5.24 | -4 | | | | | " |
| | | | | | | | | | 602 | 1.85 | -3 | 63.3 | 2.9 | 13 | | " |
| | | " | " | 760 | - | - | " | " | 625 | 7.2 | -3 | | | | | (24) |
| | | | | | | | | | 650 | 2.2 | -2 | 63 | 3.2 | 13 | | " |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Amount of addend | Rate measured | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6.1 | $C_3H_8 \rightarrow C_3H_6 + H_2 \rightarrow CH_4, C_{>4}$ (A) (B) (C) (L) (R) | anal | M/l | $A \rightleftharpoons B + C + (L + R)$ | | | | $kAB$ | 553 | 1.2 | -2 | | | | | (40) |
| | | | | A + B = 0.02 | | | | | | | | | | | | |
| | | | | C = 0.01 | | | | | | | | | | | | |
| .7 | $C_4H_{10} \rightarrow$ (a) $C_3H_6 + CH_4$; (b) $C_2H_6 + C_2H_4$; (c) $C_4H_8 + H_2$ | p | mm Hg | 760 | - | - | +p | $kA$ | 625 | 2.1 | -2 | | | | * | (24) |
| | | | | " | - | - | " | $k_1A^{1.5} + k_2A^2/(A_o - A)$ | | | | | | | * | (4) |
| | | | | | | | | $k_1$ | 480 | 1.1 | -6 | | | | | " |
| | | | | | | | | | 500 | 3.0 | -6 | | | | | " |
| | | | | | | | | | 535 | 1.4 | -5 | 58.0 | | | | " |
| | | | | | | | | $k_2$ | 480 | 3.0 | -7 | 72.0 | | | | |
| | | | | | | | | | 500 | 1.0 | -6 | | | | | |
| | | | | | | | | | 535 | 7.9 | -6 | | | | | |
| .8 | $(CH_3)_2CHCH_3 \rightarrow$ (a) $C_3H_6 + CH_4$; (b) $C_2H_6 + C_2H_4$; (c) $C_4H_8 + H_2$ | p | mm Hg | 760 | - | - | +p | $kA$ | 600 | 7.7 | -3 | | | | | (24) |
| | | | | | | | | | 625 | 2.9 | -2 | | | | | " |
| | | | | | | | | | 650 | 5.0 | -2 | | | | | " |
| | | | | 50 - 600 | | | | | | | | 64 | | | | |
| .9 | $(CH_3)_2C{:}CH_2 \rightarrow CH_4, H_2, CH_2{:}C{:}CH_2$ $(CH{:}CCH_3)$ (L) (M) (N) | anal | mm Hg | 1.3 - 20 | | +(L + M) | | $kA$ | 636 | 5.0 | -4 | | | | | (44) |
| | | | | | | | | | 686 | 3.5 | -3 | | | | | " |
| | | | | | | | | | 768 | 4.5 | -2 | | | | | " |
| | | | | | | | | | 808 | 2.2 | -1 | 67 | 5 | 12 | | " |
| .10 | $(CH_3)_2C{:}CH_2 \rightarrow CH_4, H_2, CH_2{:}CHCH_3, (CH_3)_2CHCH_3$, liquid | flow anal | mm Hg | 760 | - | - | -A | $kA$ | 600 | 1.6 | -3 | | | | | (16) |
| | | | | | | | | | 650 | 8.0 | -3 | 56 | | | | " |
| | | | | | | | | | 700 | 4.0 | -2 | | | | | " |

## SUPPLEMENTARY TABLES

**(.2.1)** $CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6, CH_3C{:}CH....$ [10]

Products in % in the outgoing gas

| °C | $100(A_o - A)/A_o$ | $C_2H_4$ | $C_2H_2$ | $C_2H_6$ | $C_3H_6$ | $CH_3C{:}CH$ | $H_2$ |
|---|---|---|---|---|---|---|---|
| 1007 | 1.27 | 0.11 | 0.04 | 0.09 | 0.02 | 0.02 | 1.91 |
| | 10.54 | 0.87 | 0.39 | 0.10 | 0.07 | 0.05 | 16.56 |
| 1033 | 1.27 | 0.13 | 0.05 | 0.09 | 0.02 | 0.03 | 1.87 |
| | 10.88 | 1.08 | 0.62 | 0.10 | 0.08 | 0.10 | 16.35 |
| | 16.91 | 1.36 | 0.68 | 0.11 | 0.09 | 0.06 | 25.32 |
| 1053 | 2.29 | 0.031 | 0.08 | 0.12 | 0.03 | 0.07 | 3.15 |
| | 9.66 | 0.98 | 0.65 | 0.14 | 0.08 | 0.14 | 14.25 |
| 1075 | 3.96 | 0.049 | 0.25 | 0.15 | 0.03 | 0.11 | 5.67 |

**(.5)** $C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_4, H_2, CH_4, R$ [41]

Time in hours; amounts of hydrocarbons in g atom C/liter; $H_2$ in M/l
Temperature 590°C

| Hours | $10^3C_2H_6$ | $10^3C_2H_4$ | $10^3H_2$ | $10^3CH_4$ | $10^3R$ |
|---|---|---|---|---|---|
| 0 | 500.00 | - | - | - | - |
| 0.5 | 44.18 | 4.16 | 4.66 | 0.95 | 0.71 |
| 1.0 | 41.76 | 4.52 | 5.42 | 2.21 | 1.51 |
| 2.0 | 37.38 | 3.54 | 5.96 | 5.43 | 3.64 |
| 3.0 | 32.78 | 3.34 | 5.44 | 8.46 | 5.42 |
| 4.0 | 31.54 | 3.16 | 5.99 | 9.54 | 5.76 |
| 5.0 | 30.16 | 2.86 | 5.84 | 10.75 | 6.23 |
| 6.5 | 28.80 | 2.62 | 5.94 | 11.94 | 6.64 |

## COMMENTS

(.1) Reaction approximately 97 % homogeneous. Induction period observed ([17]). [See, however, (.2)] Data given for *initial* rates; *k* falls with the progress of the reaction owing to retardation by $H_2$ ([14,15]); [See, however, (.2)] For that reason, also because of loss of $H_2$ by diffusion through the quartz walls, *k* is probably too low ([17]). Initial rates of ([13]) somewhat higher than those of ([17]), and show a pressure dependence not stated by ([17]). $C_2H_4$ is detected in products in flow with short time of contact at 900 - 1500° with $N_2$ as diluent ([1]). $CH_3$ radicals detected by mirror technique ([26,25]) and by mass spectography but no $CH_2$ radicals ([5]). As a function of amount of NO added, *k* seems to pass through a minimum ([13]) (see data in table), but the quantitative effect of NO is uncertain owing to an oxidation reaction ([13]). Mechanism of ([17]), $CH_4 \rightarrow H_2 + CH_2$, is unsubstantiated. Radical mechanism ([29,18]) questioned ([38]). Probably mixed molecular and short radical chains initiated by $CH_4 \rightarrow CH_3 + H$ ([26,25]). (.2) Analytical data in flow system (porcelain tube) evaluated in terms of a first-order rate constant *k* which increases systematically with increasing degree of decomposition $100(A_o - A)/A_o$. This trend is parallelled by an increase of the amounts of $C_2H_4$ and $C_2H_2$ formed among the products, as shown in the Supplementary Table (selected data). Of these two gases, $C_2H_2$ has a definite catalytic effect, $C_2H_4$ appears to have none. The upward trend of *k* seems to level off, at 1107 and 1033°C, at around 15 % decomposition. At variance with ([17]), $H_2$ 2 % increases the rate of decomposition by 20 - 30 %, and increases in particular the amounts of $C_2H_2$ and $C_2H_4$, hence no retardation effect is found; also, no induction period is observed, contrary to ([17]). $N_2$ 50 % and $H_2O$ have no effect. The data tabulated refer to a surface/volume ratio of 2.47; its increase to 9.52 increases the early rate of decomposition about 2 - 3 times; the amounts of $C_2H_2$ and $C_2H_4$ produced are increased as long as their concentrations are low, but decreased at higher concentrations, evidently owing to catalyzed decomposition at the wall. The accelerating effect of the surface disappears at 30 % decomposition. (.4) The first-order rate constants, from *initial* rates, listed in the table at close temperatures, are compiled from several sources ([32,18,43,38,19]) to show the degree of consistency of data of different authors, and by different manometric or analytical (-A, +M) methods; evidently, at

## COMMENTS *(continued)*

the initial stage, the increase of pressure is an accurate measure of the stoichiometric change as formulated. *Very close* data of different authors have been averaged and are underlined. Data of ([19]) [in brackets] are systematically too high and should, roughly, be halved to fall in line with other data listed. The first order holds only in the initial stage, and the data may be in error due to back reaction ([2]). The reaction is very nearly homogeneous. Some $CH_4$ and condensate are found in addition to $C_2H_4 + H_2$ ([32,43,3]); with further progressing reaction, $CH_4$ + condensate become increasingly the main products: see further under (.5) and (.5.1). Mirror ([27]) and mass-spectrographic ([5]) techniques show $CH_3$ and $C_2H_5$ radicals. Para-ortho-$H_2$ system shows H atoms ([21]). The decomposition is only weakly sensitized by $CH_3$ radicals ([34,4]). Selected data on inhibition by NO are from ([35]) and ([36]); there is evidence of oxidation by NO ([12]). The reaction appears to be only partly a chain process. **(.5) (.5.1)** The rate laws and rate constants are derived from complete analyses for $C_2H_6$, $C_2H_4$, $H_2$, $CH_4$, and condensate $R(C_{>4})$, as illustrated by the Supplementary Table for the decomposition of initially pure $C_2H_6$, 0.025 M/l, at 590°C. The *initial* rate constants for production of $CH_4$ and for production of R are derived from this table. The process is conceived as built around the "background reaction" $C_2H_6 \rightleftharpoons C_2H_4 + H_2$, with the production of $CH_4$ and of R possibly representable by the stoichiometric equation $C_2H_6 + C_2H_4 + H_2 \rightarrow 2CH_4 + C_2H_4$, followed by polymerization of $C_2H_4$. Starting with pure $C_2H_6$ (.5), the rates are initially self-accelerating up to a breaking point lying roughly close to but not at the equilibrium composition. During the first 3 hours, $k$ for the production of R oscillates but shows no systematic trend, whereas $k$ for the production of $CH_4$ falls from $1.4 \times 10^{-2}$ to $5.4 \times 10^{-3}$. Packing of the reaction vessel results in a behavior resembling the case of a near equilibrium mixture. The data under (.5.1) refer to a $C_2H_6 + C_2H_4 + H_2$ mixture initially close to the equilibrium composition. In this case, after pretreatment with $H_2$, increase of the surface is without effect, but some surface effect appears at high $H_2$ pressures. A mechanism proposed by ([39]) to account for the $k$AB law, and involving formation of an intermediate molecular compound AB as rate determining step, is unsubstantiated. **(.6)** Data of ([37]) between 550 and 600°, and data of ([24]) up to 650°C, are given as representative. The rate constants ([37]) are extrapolated from the experimental pressure range (50 - 600 mm Hg) to "infinite"

## COMMENTS *(continued)*

pressure. The $k$ of ([22]). ([19]), and ([8]) at 575°C are close to ([37]), and so are the arrhenian constants $E$ and $A$ of ([19]), but those of ([22]) are distinctly higher. Products at 10 % decomposition at 575°C under 739 mm Hg are $C_3H_6$ 23.6, $H_2$ 22.4, $C_2H_4$ 23.2, $CH_4$ 28.0, $C_2H_6$ 2.8 % ([37]); analyses of ([8]) are in excellent agreement therewith. The change of pressure appears to be a sufficiently accurate measure of the conversion as represented by the stoichiometric formulation given, with (a) and (b) in the ratio 1:1; at later stages of the reaction, the simple stoichiometric formulation is no longer valid. The first-order $k$ fell strongly in the course of a single run and with decreasing initial pressure ([24,2,37]); thus, between 760 and 2 mm Hg, $k$ falls to about one-half; dilution with $N_2$ increases $k$ only slightly ([24]). The reaction is essentially homogeneous ([24]). The reaction is sensitized by radicals from azomethane ([34]) and from ethylene oxide ([4]); it is inhibited by NO ([13]) and by $C_3H_6$ ([31]). $CH_3$ radicals detected by mirror technique ([6]); H atoms detected by ortho-para-$H_2$ conversion ([20]). Probably mixed molecular and short radical- chain mechanism. Further literature ([23,9,33]).

(.7) The simple first-order $k$ applicable to the initial rate, is given for comparison with other hydrocarbons. At pressure reduced to 2 mm Hg, $k$ falls by less than 50 %. The two-term law holds over a more extended range of the reaction. The ratio (a):(b):(c) = 3:2:1 at 25 % decomposition. The reaction is essentially homogeneous. It is sensitized by radicals from ethylene oxide ([4,36]), $C_3H_6$ ([4,31,36]), $Hg(CH_3)_2$ ([7]) and azomethane ([36]), inhibited by NO ([4,36]) but the inhibition is transitory, the rate becoming normal after about 15 % conversion ([4]). NO does not completely suppress chains in sensitized reaction ([36]). Mirror technique shows presence of $CH_3$ radicals ([6,30]). Probably chain mechanism involving a large number of short chains ([36]). (.8) Essentially homogeneous. The initial first-order $k$ given fell rapidly with the progress of the reaction. At pressure reduced to 2 mm Hg, $k$ falls to about 1/5 of its value under 760 mm Hg. Dilution with $N_2$

## COMMENTS *(continued)*

increases $k$ only very slightly. The ratio (a):(b):(c) is about 15:1:35 at the initial stage. Further literature ([23, 8, 22, 37]). **(.9)** Proposed mechanism:

$A \rightarrow CH_2{:}C(CH_3)CH_2 + H$;

$H + A \rightarrow CH_2{:}C(CH_3)CH_2 + H_2$;

$CH_2{:}C(CH_3)CH_2 \rightarrow CH_2{:}C{:}CH_2 + CH_3$;

$CH_3 + A \rightarrow CH_2{:}C(CH_3)CH_2 + CH_4$;

$CH_2{:}C(CH_3)CH_2 + CH_3 \rightarrow CH_2{:}C(CH_3)CHCH_3$.

Chain length about 9 ([44]). **(.10)** Homogeneous; $k$ reasonably constant with variation of contact time by a factor of 2 - 3, and with variation of A (dilution by $H_2$ or $N_2$) by a factor of 2. The liquid is 20 - 60 % by weight of A decomposed.

## LITERATURE

(1) F. de Budder, H.Biederman, *BSC* 1930, **47**, 704. (2) A.I.Dintzes, A.V.Frost, *ZOK* 1933, **3**, 747. (3) A.I.Dintzes, V.R.Zharkova, A.V.Zherko, A.V.Frost, *ZOK* 1937, **7**, 1063, 1754. (4) L.S.Echols, R.N.Pease, *ACS* 1936, **58**, 1317; 1939, **61**, 208, 1024. (5) G.C.Eltenton, *JCP* 1942, **10**, 403. (6) B.L.Evering, *ACS* 1939, **61**, 1400. (7) F.E.Frey, *IEC* 1934, **26**, 198. (8) F.E.Frey, H.J.Hepp, *IEC* 1933, **25**, 441. (9) F.E.Frey, D.F.Smith, *IEC* 1928, **20**, 948.

(10) A.S. Gordon, *ACS* 1948, **70**, 395. (12) J.T. Gray, M.W.Travers, F.T. White, *PRS*[A] 1938, **167**, 15. (13) J.E.Hobbs, C.N.Hinshelwood, *PRS*[A] 1938, **167**, 447. (14) G.C.Holiday, H.C.Exell, *CSL* **1929**, 1066. (15) G.C.Holiday, W.J.Gooderham, *CSL* **1931**, 1594. (16) C.D.Hurd, L.L.Spence, *ACS* 1929, **51**, 3561. (17) L.S.Kassel, *ACS* 1932, **54**, 3949; 1935, **51**, 833. (18) L. Kuchler, H. Theile, *ZPC*[B] 1939, **42**, 359. (19) L.F.Marek, W.B. McCluer, *IEC* 1931, **23**, 878.

(20) F.Patat, *ZPC*[B] 1936, **32**, 274. (21) F.Patat, H.Sachsee, *ZEC* 1935, **41**, 493. (22) R.E.Paul, L.F.Marek, *IEC* 1934, **26**, 454. (23) R.N.Pease, *ACS* 1928 **50**, 1779. (24) R.N. Pease, E.S. Durgan, *ACS* 1930, **52**, 1262. (25) F.O.Rice, *ACS* 1939, **61**, 213. (26) F.O.Rice, M.D.Dooley, *ACS* 1934, **56**, 2747. (27) F.O.Rice, D.M.Dooley, *ACS* 1933, **55**, 4245. (28) F.O.Rice, W.S.Haynes, *ACS* 1948, **70**, 964. (29) F.O.Rice, K.F.Herzfeld, *ACS* 1934, **56**, 284, *JCP* 1939, **7**, 671.

(30) F.O. Rice, W.R. Johnston, B.L. Evering, *ACS* 1932, **54**, 3529. (31) F.O. Rice, O.L. Polly, *JCP* 1938, **6**, 273. (32) H.Sachsee, *ZPC*[B] 1935, **31**, 87. (33) V.Schneider, P.K.Frolich, *IEC* 1931, **23**, 1405. (34) D.V.Sickman, O.K.Rice, *JCP* 1936, **4**, 608. (35) L.H.K.Staveley, *PRS*[A] 1937, **162**, 557. (36) E.W.R.Steacie, H.O.Folkins, *CJR*[B] 1939, **17**, 105; 1940, **18**, 1. (37) E.W.R.Steacie, I.E.Puddington, *CJR*[B] 1938, **16**, 411. (38) E.W.R.Steacie, G.Shane, *CJR*[B] 1940, **18**, 203, 351. (39) M.W.Travers, *TFS* 1937, **33**, 735.

## LITERATURE *(continued)*

(40) M.W.Travers, *TFS* 1937, **33**, 751. (41) M.W.Travers, T.J.P.Pearce, *SCI* 1934, **53**, 321. (42) H.H.Storch, *ACS* 1932, **54**, 4185. (43) H.H.Storch, L.S.Kassel, *ACS* 1937, **59**, 1240. (44) M.Szwarc, *JCP* 1949, **17**, 292.

# PYROLYSIS

## Aromatic Hydrocarbons

*Gas phase*

Amounts are in mm Hg.
Rates are in mm Hg per sec.

| No. | Reaction | Amount of reactant | Rate measured | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ |
| .1 | $o\text{-}C_6H(CH_3)_2 \longrightarrow H_2,\ CH_4,\ C_6H_5,\ o,o'\text{-}CH_3C_6H_4CH_2CH_2C_6H_4CH_3$ | 3 - 4 | $+d(H_2 + CH_4)$ | $kA$ | 730 | 3.8 | -3 | | | |
| | | | | | 788 | 3.1 | -2 | | | |
| | | | | | 815 | 7.0 | -2 | | | |
| | | | | | 838 | 1.47 | -1 | 74.8 | 5 | 13 |

## COMMENTS

Flow system. About 10 % of A is decomposed into $C_2$ hydrocarbons. The products are interpreted by the reaction mechanism: $A \longrightarrow o\text{-}C_6H_4(CH_3)CH_2 + H$ (rate determining); $H + A \longrightarrow H_2 + o\text{-}C_6H_4(CH_3)CH_2$, or $H + A \longrightarrow CH_3 + C_6H_5CH_3$; $CH_3 + A \longrightarrow CH_4 + o\text{-}C_6H_4(CH_3)CH_2$; $2\ o\text{-}C_6H_4(CH_3)CH_2 \longrightarrow o,o'\text{-}CH_3C_6H_4CH_2CH_2C_6H_4CH_3$.

## LITERATURE

M. Szwarc, *JCP* 1948, **16**, 128.

942151 O—51——35

# PYROLYSIS

## Alicyclic hydrocarbons

**Homogeneous Reactions**
**571.413.**

Rate measured: $+\Delta p$

*Gas phase*

Amounts are in mm Hg.
Rates are in mm Hg per sec.

| No. | Reaction | Method | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | *cyclo*-$C_6H_{12} \rightarrow H_2$ + *cyclo*-$C_6H_{10} \rightarrow H_2 + C_2H_4 + C_4H_6$ | $p$ | 10 – 200 | $k\,A$ | 485 – 565 | | | 60 | 5 | 11 | * | (1) |
| .2 | *cyclo*-$C_6H_{10} \rightarrow C_2H_4 + C_4H_6$ | $p$ | 10 – 200 | $k\,A$ | 485<br>485 – 565 | 7 | −4 | 57.5 | 8.9 | 12 | * | (1) |
| .3 | *cyclo*-$C_5H_9 \cdot CH_3 \rightarrow H_2 + C_2H_4 + C_4H_6$ | $p$ | 10 – 150 | $k\,A^{1.3}$ | 485 – 565 | | | 60 | 3.2 | 11 | * | (1) |

## COMMENTS

(.1) Total pressure change 2.4. Side reaction $A \rightarrow 2C_3H_6$; no isomerization to *cyclo*-$C_5H_9CH_3$. Induction period not due to that isomerization, contrary to (2). $H_2$ has no marked effect; NO has no effect. (.2) The equation represents 80 – 90 % of the reaction. Proof of homogeneity given. $H_2$ has little effect, reduces the rate only in large amounts; NO has no effect. (.3) Induction period. Total pressure change 2.5.

## LITERATURE

(1) L. Küchler, *TFS* 1939, 35, 874. (2) R. N. Pease, Norton, *ACS* 1933, 55, 3190.

**Homogeneous Reactions**
**571.441.**

Amounts are in mm Hg.
Rates are in mm Hg per sec.

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Aldehydes** | | | | | | | | | | | | | | | | |
| .1 | $HCHO \rightarrow H_2 + CO$ | p | 30 - 370 | | | +p | $kA^2$ | 510 | | | 3.6 | -6 | | | | * | (3) |
| | | | | | | | | 569 | | | 2.7 | -5 | | | | | |
| | | | | | | | | 607 | | | 9.0 | -5 | 45 | | | | |
| .2 | $CH_3CHO \rightarrow CH_4 + CO$ | p, anal | 50 - 450 | | | -A | $kA^2/A_o^{1/2}$ | | | | | | | | | * | (17) |
| | | | | | | | | 450 | | | 4.8 | -6 | | | | | |
| | | | | | | | | 477 | | | 1.4 | -5 | | | | | |
| | | | | | | | | 512 | | | 4.8 | -5 | | | | | |
| | | | | | | | | 542 | | | 1.5 | -4 | | | | | |
| | | | | | | | | 577 | | | 5.0 | -4 | 46 ±0.5 | 2.5 | 8 | | |
| .3 | $CH_3CHO \rightarrow CH_4 + CO$ | p, anal | A = 37 - 172 | | | -A | $kA^{3/2}[A + b(L + M)]^{1/2}/[A + b'(L + M)]^{1/2}$ | | | | | | | | | * | (17) |
| | | | L + M = 322 + 183 | | | | | 577 | | $k$ | 5.0 | -4 | | | | | |
| | | | | | | | | | | $b$ | 6.0 | -2 | | | | | |
| | | | | | | | | | | $b'$ | 3.3 | -1 | | | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $CH_3CHO \rightarrow CH_4 + CO$ | p, anal | 75 - 225 | $O_2$ | < 0.05 | -A | $kA^{3/2} + k'A^{3/2}[O_2]$ | | | | | | | | | | (18) |
| | | | | | | | | 450 | | $k$ | 4.8 | -6 | | | | | |
| | | | | | | | | " | | $k'$ | 7.5 | -3 | | | | | |
| | | | | | | | | 477 | | $k$ | 1.4 | -5 | | | | | |
| | | | | | | | | " | | $k'$ | 6.4 | -3 | | | | | |
| | | | | | | | | 512 | | $k$ | 4.8 | -5 | | | | | |
| | | | | | | | | " | | $k'$ | 4.3 | -3 | | | | | |
| .5 | $CH_3CHO \rightarrow CH_4 + CO$ | p, (anal) (thc) | 5 - 100 | $H_2$ | 0 - 400 | | $kA^{3/2} + k'A^{1/2}[H_2]$ | | | | | | | | | * (9) | (10) |
| | | | | | | -A | | 556 | | $k$ | 3.3 | -4 | 49.5 | | | | " |
| | | | | | | | | | | $k'$ | 5 | -5 | | | | | |
| | | | | | | | | | | (0.5) | | | | | | | |
| | | | 17 | | 100 | | | 556 | 0.04 | 5.2 | | | | | | | " |
| | | | 100 | | 424 | | | " | 0.55 | 2.2 | | | | | | | |
| | | | 175 | | 0 | | | 518 | | 12.1 | | | | | | | " |
| | | | " | | 400 | | | " | | 9.1 | | | | | | | |
| | | | " | | 800 | | | " | | 7.2 | | | | | | | |
| .6 | $CH_3CHO \rightarrow CH_4 + CO$ | p | 25 - 330 | $N_2O$ | 100 | +p | $kA$ | 480 | (0.5) | 155 | | | 27 | | | * | (37) |
| | | | 100 | " | 100 | $kA^{3/2}[N_2O]^{1/2}$ | | 460 | " | 2600 | | | | | | | " |
| | | | | | | | | 520 | | 335 | | | 40 | | | | |
| .7 | $CH_3CHO \rightarrow CH_4 + CO$ | p | 100 | NO | 100 | $kA^{3/2}[NO]$ | | 450 | " | 1280 | | | | | | * | (38) |
| | | | | | | | | 470 | | 645 | | | | | | | |
| | | | | | | | | 480 | | 400 | | | | | | | |
| | | | | | | | | 505 | | 180 | | | 37.3 | | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | (0.5) | | | | | | | |
| .8 | $CH_3CHO \rightarrow CH_4 + CO$ | p | 50 | $C_3H_6$ | ∞ | +p | $kA^{\sim 2}$ | 550 | | 1400 | | | | | | * | (28a) |
| | | | 75 | " | " | | | | | | | | 48 | | | | |
| | | | 200 | " | 0 | " | | 550 | | 210 | | | | | | | " |
| | | | " | | 5 | | | " | | 290 | | | | | | | |
| | | | " | | 50 | | | " | | 480 | | | | | | | |
| | | | " | | ∞ | | | " | | 600 | | | | | | | |
| | | | 200 | " | ∞ | " | " | 515 | | 2300 | | | | | | | " |
| | | | " | | " | | | 570 | | 340 | | | 46 | | | | |
| | | | " | | " | | | | | | | | | | | | |
| | | | 350 | " | ∞ | " | " | | | | | | 47 | | | | " |
| | | | 400 | " | ∞ | " | " | 550 | | 350 | | | | | | | " |
| | | | | | | | | | (× $10^3$) | (0.5) | | | | | | | |
| .9 | $CH_3CHO \rightarrow CH_4 + CO$ | p | | | | +p | | | | | | | | | | | |
| | | | 50 | | | | | 535 | 1.16 | 670 | | | 55.2 | | | * | (28) |
| | | | 400 | | | | | " | 3.83 | 230 | | | 49.1 | | | | |
| | | | 50 | | | " | | 515 | | 2135 | | | | | | | " |
| | | | " | | | | | 575 | | 182 | | | | | | | |
| | $CD_3CDO \rightarrow CD_4 + CO$ | " | 50 | | | " | | 535 | 0.40 | 1700 | | | 56.4 | | | * | " |
| | | | 400 | | | | | " | 1.57 | 450 | | | 49.7 | | | | |
| | | | 50 | | | " | | 511 | | 6065 | | | | | | | " |
| | | | " | | | | | 571 | | 515 | | | | | | | |
| .10 | $CH_3CHO \rightarrow CH_4 + CO$ | p | 107 | | | +p | | 484 | 0.018 | | | | | | | * | (20) |
| | | | 186 | | | | | " | 0.035 | | | | | | | | |
| | | | 328 | | | | | " | 0.087 | | | | | | | | |
| | | | 313 | | | | | 542 | 0.67 | | | | | | | | |

571.441.

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .10 | *(continued)* | | | | | | | | | | | | | | | | |
| | $CD_3CDO \rightarrow CD_4 + CO$ | p | 293 | | | +p | | 484 | 0.052 | | | | | | | * | (20) |
| | | | 70 | | | | | 542 | 0.057 | | | | | | | | |
| | | | 210 | | | | | " | 0.31 | | | | | | | | |
| | | | 302 | | | | | " | 0.56 | | | | | | | | |
| .11 | $C_2H_5CHO \rightarrow CO, C_2H_6, H_2, CH_4, C_nH_{2n}$ | p | 50 | | | +p | | 550 | (0.5) | 240 | | | 63.5 | | | * | (28a) |
| | | | 160 | | | | | " | | 180 | | | 61 | (509 - 589°) | | | (40a) |
| | | | 300 | | | | | " | | 150 | | | 56 | | | | |
| | | | 50 | $C_3H_6$ | 50 | " | | 550 | | 420 | | | | | | | (28a) |
| | | | 300 | | " | | | " | | 190 | | | | | | | |
| | | | 50 | | 200 | | | " | | 360 | | | | | | | |
| | | | 300 | | " | | | " | | 230 | | | | | | | |
| | | | 300 | NO | 1.0 | " | | 550 | | 200 | | | | | | | |
| | | | " | | 6.0 | | | " | | 250 | | | | | | | |
| | $C_2H_5CHO \rightarrow CO + C_2H_6$ | | 70 - 270 | $I_2$ | 2 - 30 | $kA[I_2]/(1+bA)$ | | 336 | | $k$ | 7.6 | -4 | | | | * | (1a) |
| | | | | | | | | 385 | | | 9.15 | -3 | 33.5 | 1 | 9 | | |
| | | | | | | | | | | $b$ | 7.8 | -3 | | | | | |
| .12 | $CH_2{:}CHCHO \rightarrow CO + (CH_4, C_2H_6 + H_2, C_2H_4, C_4H_8)$ | | | | | | | | | | | | | | | | |
| | | p (anal) | 20 | | | +p | $kA^{<2}$ | 508 | (0.5) | 1031 | | | | | | * | (35) |
| | | | 100 | | | | | " | | 408 | | | | | | | |
| | | | 300 | | | | | " | | 167 | | | | | | | |
| | | | 30 | | | " | " | 520 | | 690 | | | | | | | " |
| | | | 100 | | | | | " | | 286 | | | | | | | |
| | | | 300 | | | | | " | | 520 | | | | | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .12 | $CH_2{:}CHCHO \rightarrow CO + (CH_4,\ C_2H_6 + H_2,\ C_2H_4,\ C_4H_8)$ *(continued)* | | 30 | | | +p | $kA^{<2}$ | 540 | | 364 | | | 42.2 | | | | (35) |
| | | | 100 | | | | | " | | 156 | | | 40.7 | | | | |
| | | | 300 | | | | | " | | 68 | | | 36.5 | | | | |
| | **Ketones** | | | | | | | | | | | | | | | | |
| .13 | $CH_3COCH_3 \rightarrow CH_4 + CH_2{:}CO$ | p | 127 | | | +p | $kA$ | 553 | | | 1.1 | -3 | | | | * | (13) |
| | | | 61 | | | | | " | | | 9.5 | -3 | | | | | |
| | | | 6 | | | | | " | | | 5.1 | -4 | 63 | 1 | 15 | | |
| | | p | 400 | | | +p | $kA$ | 570 | | | 3.0 | -3 | | | | | (42) |
| | | | " | | | | | 600 | | | 7.3 | -3 | | | | | |
| | | | " | | | | | 610 | | | 1.2 | -2 | | | | | |
| | | | " | | | | | 620 | | | 1.8 | -2 | 68 | 8 | 14 | | |
| | | p | >100 | | | -A | $kA$ | 600 | | | 7.3 | -3 | | | | | |
| | | | 55 | | | | | " | | | 5.3 | -3 | | | | | |
| | | | 8 | | | | | " | | | 3.0 | -3 | | | | | |
| | | | 2.5 | | | | | " | | | 2.3 | -3 | | | | | |
| | | | 100 | $C_3H_6$ | 100 | -A | $kA$ | 570 | | | 5.3 | -4 | | | | * | (29) |
| | | | | | " | | | 600 | | | 1.9 | -3 | | | | | |
| | | | | | " | | | 615 | | | 3.6 | -3 | 62.6 | | | | |
| | | | " | " | ∞ | " | " | 570 | | | 4.1 | -4 | | | | | |
| | **Ethers** | | | | | | | | | | | | | | | | |
| .14 | $CH_3OCH_3 \rightarrow CH_4 + HCHO \rightarrow CH_4 + H_2 + CO$ | p | 400 - 900 | | | +p | $kA$ | 422 | | | 4.5 | -6 | | | | * | (9) |
| | | | | | | | | 478 | | | 1.27 | -4 | | | | | (30) |
| | | | | | | | | 552 | | | 4.3 | -3 | 58.5 | | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .14 | $CH_3OCH_3 \rightarrow CH_4 + HCHO \rightarrow CH_4 + H_2 + CO$ *(continued)* | p | 400 - 900 | NO | >1 | +p | *k* A | 537 | | | 2.3 | -4 | | | | * | (30) |
| | | | | | | | | 565 | | | 9.0 | -4 | | | | | " |
| | | | | | | | | 580 | | | 1.8 | -3 | 62 | | | | |
| .15 | $CH_3OC_2H_5 \rightarrow CH_4 + CH_3CHO \rightarrow 2\ CH_4 + CO$ | p | 380 | | | +p | | 460 | (0.25) | 3220 | | | | | | * | (34) |
| | | | 720 | | | | | " | | 2500 | | | | | | | |
| | | | 85 | | | | | 480 | | 2120 | | | | | | | |
| | | | 320 | | | | | " | | 1290 | | | | | | | |
| | | | 720 | | | | | " | | 880 | | | | | | | |
| | | | 80 | | | | | 500 | | 880 | | | | | | | |
| | | | 570 | | | | | " | | 440 | | | | | | | |
| | | | ∞ | | | | | | | | | | 55 | | | | |
| | | p | 297 | | | +p | *k* A | 457 | (0.25) | 9084 | | | | | | * | (36) |
| | | anal | " | | | | | " | (0.5) | 22656 | ~ 3 | -5 | | | | | |
| | | | 250 | | | | | 487 | (0.25) | 1716 | | | | | | | |
| | | | " | | | | | " | (0.5) | 4002 | ~ 2 | -4 | | | | | |
| | | | 299 | | | | | 509 | (0.25) | 828 | | | | | | | |
| | | | " | | | | | | (0.5) | 2058 | ~ 6 | -4 | 65 | | | | |
| | | " | 270 | $C_2H_5I$ | 0.6 | +p | *k* A | 480 | (0.5) | 550 | ~ 2 | -3 | | | | * | (36) |
| | | | 250 | | 0 | | | 487 | | 4002 | ~ 2 | -4 | | | | | |
| | | | 241 | | 25 | | | " | | 68 | | | | | | | |
| | | " | 50 - 300 | $I_2$ | 7 | +p | *k* A | 460 | (0.25) | 990 | 1.4 | -3 | | | | * | (2) |
| | | | | | | | | 504 | | 230 | 6.1 | -3 | | | | | |
| | | | | | | | | 547 | | 63 | 2.2 | -2 | 37.5 | | | | |
| | | " | 100 | NO | 0 | +p | | 560 | (0.25) | 65 | | | | | | * | (33) |
| | | | | | 0.1 | | | " | | 230 | | | | | | | |
| | | | | | 1 | | | " | | 475 | | | | | | | |
| | | | | | 10 | | | " | | 400 | | | | | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .15 | $CH_3OC_2H_5 \rightarrow CH_4 + CH_3CHO \rightarrow 2\ CH_4 + CO$ *(continued)* | p anal | 400 | NO | 5 | +p | | 523 | (0.25) | 1400 | | | | | | * | (33) |
| | | | | | " | | | 560 | | 270 | | | | | | | |
| | | | | | " | | | 600 | | 48 | | | 62 | | | | |
| .16 | $CH_3OC_3H_7 \rightarrow C_2H_6 + CH_4 + CO$ | p | 20 - 240 | | | +p | $k$ A | 400 | (0.5) | 846 | 8.2 | -4 | | | | * | (6) |
| | | | | | | | | 450 | | 62 | 1.1 | -2 | 49 | 1 | 11 | | |
| .17 | $CH_3OCH(CH_3)_2 \rightarrow CH_4 + CH_3COCH_3$; $HCHO + C_3H_8$; $H_2 + CO + C_3H_8$ | p | 100 - 300 | $I_2$ | 7 | +p | $k$ A | 453 | | | 2.6 | -3 | | | | | (2) |
| | | | | | | | | 490 | | | 6.9 | -3 | | | | | |
| | | | | | | | | 518 | | | 1.4 | -2 | 29.5 | | | | |
| .18 | $CH_2{:}CHOC_2H_5 \rightarrow C_2H_4 + CH_3CHO$ | p | 50 - 190 | | | +p | $k$ A | 389 | (0.2) | 265 | 6.0 | -3 | | | | * | (39) |
| | | | | | | | | 412 | | 88 | 1.8 | -2 | | | | | |
| | | | | | | | | 424 | | 47 | 3.4 | -2 | 44.4 | 4.0 | 11 | | |
| .19 | $(CH_3)_2CHOCH(CH_3)_2 \rightarrow CH_4,\ CO,\ C_nH_{2n}$ | p | 30 - 330 | | | +p | $k$ A | 551 | | | 6.3 | -3 | | | | * | (7) |
| | | | | | | | | 566 | | | 1.3 | -2 | 63 | | | | |
| .20 | $(CH_3)_2CHOCH(CH_3)_2 \rightarrow C_3H_8 + CH_3COCH_3$ | p | 94 | $I_2$ | 25 | +p | $k$ A | 400 | | | 1.3 | -2 | 29.0 | | | | (7) |
| | **Peroxides** | | | | | | | | | | | | | | | | |
| .21 | $(CH_3)_3COOC(CH_3)_3 \rightarrow 2\ CH_3COCH_3 + C_2H_6$ | anal | | | | +M | $k$ A | 129 | | | 2.0 | -5 | | | | * | (34a) |
| | | | | | | | | 138 | | | 4.3 | -5 | | | | | |
| | | | | | | | | 150 | | | 1.4 | -4 | | | | | |
| | | | | | | | | 152 | | | 1.6 | -4 | | | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | Initial rate | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .21 | $(CH_3)_3COOC(CH_3)_3 \rightarrow 2\ CH_3COCH_3 + C_2H_6$ *(continued)* | | | | | | | | | | | | | | | | |
| | $(CH_3)_3COOC(CH_3)_3 \rightarrow 2\ CH_3COCH + 2\ CH_3$; $CH_3 + C_6H_5CH_3 \rightarrow C_6H_5CH_2 + CH_4$ (M); $CH_3 + CH_3 \rightarrow C_2H_6$ (M′) $2\ C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5$ | anal | 10 - 40 (total) | $C_6H_5CH_3$ | | +(M + M′) | $kA$ | 116 | | | 5.1 | -6 | | | | * | [34a] |
| | | | | | | | | 125 | | | 8.5 | -6 | | | | | |
| | | | | | | | | 144 | | | 6.0 | -5 | | | | | |
| | | | | | | | | 148 | | | 9.0 | -5 | | | | | |
| | | | | | | | | 155 | | | 1.9 | -4 | | | | | |
| | | | | | | | | 167 | | | 6.1 | -4 | 34 | 2 | 13 | | |
| .22 | $(CH_3)_3COOC(CH_3)_3 \rightarrow (CH_3)_2CO,\ CH_3COC_2H_5,\ CH_4$ | p anal | 50 - 380 | $N_2$ | ~ 5 | +p | $kA$ | 147.2 | | | 1.4 | -4 | | | | * | [21a] |
| | | | | | | | | 154.6 | | | 3.2 | -4 | 39 | 3.2 | 16 | | |
| .23 | $(C_2H_5)(CH_3)_2COOC(CH_3)_2(C_2H_5) \rightarrow$ | p anal | 70 - 150 | $N_2$ | ~ 5 | +p | $kA$ | 132.2 | | | 7.2 | -5 | | | | * | [21a] |
| | | | | | | | | 149.7 | | | 4.8 | -4 | 37 | | | | |

## COMMENTS

(.1) At higher concentrations of the products the reaction tends to become first-order; $k$ is only approximate owing to simultaneously occurring condensation reactions.

(.2) - (.10) $CH_3CHO \rightarrow CH_4 + CO$.

(.2) - (.3) The data of Letort (.2,.3) [17,18] valid in rigorous absence of $O_2$ ($<10^{-5}$ vol %) and on a surface poisoned by the decomposition products, are rated most reliable; (.1) holds in the initial stage, (.2) in the presence of considerable amounts of products. The retardation by the products, expressed by the rate law (.3), is the same whether caused by $CH_4$, CO, or their sum; apparent evidence to the contrary [11] is unreliable owing to disregard of sensitivity to surface treatment. The increase of the rate caused by the products [27] is for the heterogeneous reaction of condensation. The data(selected points) are recalculated to mm Hg and sec; in units of M/l and sec, the rate constant of law (.2) is $k = 7.37 \times 10^{10} e^{-46000/T}$ Analysis for $CH_3CHO$ during a run [41] confirms the manometric data which show 96 - 98.5 % total pressure change. Large surface/volume ratio [27] or clean wall surface [17] give abnormally high rates of high apparent order and new products (CO, $H_2O$, propene polymer). Empirically, the order in $CH_3CHO$ during one run, as far as it can be established, might perhaps best be approximated by 1.8, varying with the nature and condition of the surface [17,11,14,10]. From one run to another, the order in the initial concentration of $CH_3CHO$ is 1.5 in the range 0.3 - 1160 mm Hg [17,11,14,10]. The alleged variation of $E$ with the pressure [4] is not substantiated if $E$ is, correctly, calculated from $k$ instead of from the half-lives.

The empirical rate law (.3) is obtained by the following mechanism of molecular activation $\rightleftharpoons$ deactivation and $CH_3$ and H radical chains [17]:

$$(1 \rightleftharpoons 1') \quad A + A \rightleftharpoons A^* + A$$
$$(2 \rightleftharpoons 2') \quad A + L \rightleftharpoons A^* + L$$
$$(3 \rightleftharpoons 3') \quad A + M \rightleftharpoons A^* + M$$
$$(4) \quad A^* \rightarrow CH_3 + H$$
$$(5) \quad CH_3 + A \rightarrow L + M + CH_3$$
$$(6) \quad H + A \rightarrow M + H_2 + CH_3$$
$$(7) \quad CH_3 + CH_3 \rightarrow C_2H_6$$

If $k_2 = k_3$ and $k'_2 = k'_3$, one has $k = k_5 k_1 k_4 / k'_1 k_7^{1/2}$, and $b = k_2/k_1$; $b' = k'_2/k'_1$.

(.4) Selected values from [18] rated highly reliable; $k$ and $k'$ are calculated from *initial* rates, converted to sec; $k$ is in complete agreement with (.2 - .3). The accelerating effect of $O_2$ ceases somewhat abruptly after a time and residual $CH_3CHO$ decomposes approximately as pure $CH_3CHO$. The amount decomposed per $O_2$ varies from 1000 to 4000 as vol % $O_2$ decreases from 0.015 to 0.0004. The temperature

coefficient of $k'$ is negative. The first order with respect to $O_2$ and the independence of the rate of the surface/volume ratio are confirmed by ([37]). (.5) Selected data given as probably moderately accurate empirical material, but the original rate constants, derived from the half-lives on assumption of a rate law $kA^2 + k'A[H_2]$, evidently superseded by the work of ([17]) and the laws (.2 - .4) are omitted. With the rate law tentatively included in the table (by the editors), $k$, from *initial* rates at 556° C, is fairly consistent with the values of ([17]), The ratio $k'/k \sim 0.1$, as in the original. No attempt was made to derive $k$ values from half-lives. (.6) Selected data given as empirical material. First order in $CH_3CHO$ obtains in clean vessels for the *initial* rates from one run to another, but the order within one run is more nearly 1.5. The rate rises with $[N_2O]$ up to a limit for $N_2O/CH_3CHO = 2.5$. The 1.5 order in $CH_3CHO$ and the 0.5 order in $N_2O$ are found with wall covered with carbon. Suggested mechanism (not substantiated):

$$A + N_2O \longrightarrow N_2 + CH_3CO + OH$$
$$OH + A \longrightarrow CH_3CO + H_2O$$
$$CH_3CO \longrightarrow CH_3 + CO$$
$$CH_3 + A \longrightarrow CH_4 + CH_3CO$$
$$CH_3 + CH_3 \longrightarrow C_2H_6$$

(.7) Rate roughly proportional to [NO] in the presence of excess NO. Positive catalysis by NO at higher pressures but slight inhibition by small amounts of NO is also asserted by ([28a]). The reality of the effect, on account of possible contamination with $O_2$, is doubtful. The reaction is more rapid on carbon-covered surface and then increase of the surface area has little effect. (.8) Increasing amounts of $C_3H_6$ cause increasing inhibition; $C_3H_6 = \infty$ designates the amount of $C_3H_6$ producing extrapolated *maximum inhibition*, it being claimed that very large amounts of $C_3H_6$ exert positive catalysis; not substantiated. At maximum inhibition ($C_3H_6 = \infty$), it is claimed that $E$ varies somewhat with the initial ($CH_3CHO$), thus, at 75, 200, and 350 mm Hg, $E$ = 48, 46, and 47 kcal. Approximately second-order in $CH_3CHO$ for the completely inhibited reaction. The maximum inhibition by $C_3H_6$ is interpreted as suppression of the chain part of the reaction, with only the molecular-rearrangement part subsisting (see further comment .10). (.9) Selected data as empirical material in view of comparison of $CH_3CHO$ and $CD_3CDO$. No rate law or constants derivable. Degree of reliability from the point of view of absence of $O_2$ and wall condition uncertain. See the following comment (.10). (.10) The selected *initial* rates of ([20]) included in the table were obtained with $CH_3CHO$ treated by distillation over crystals of hydroquinone to ensure removal of $O_2$. These are compared with initial rates calculated from data of ([28]) (.9) and ([28a]) (.8), (by assuming an 1.6 order in $CH_3CHO$ and the corresponding $k$ from the half-lives), and with data of ([17]) calculated from his Arrhenian equation (.2). It develops that the initial rates of ([20]) for the treated $CH_3CHO$, consider-

ed to be the "true" rates, are lower than the uninhibited rates of ([28a]), higher than the completely inhibited ($C_3H_6 = \infty$) rates, and up to 25 % lower than the initial rates of ([17]); this, if anything, can be taken as a confirmation of the reliability of the data of ([17]). With $CH_3CHO$ not treated by distillation over hydroquinone, the rates are higher throughout, no doubt due to catalysis by traces of $O_2$.

Infrared analysis showed absence of formation of mixed deuteromethanes when "treated" $CH_3CHO$ and $CD_3CDO$ are heated together; on the assumption that $CH_3$ and $CD_3$ radicals would necessarily react according to $CH_3 + CD_3CDO \longrightarrow CH_3D + CD_3 + CO$ and $CD_3 + CH_3CHO \longrightarrow CD_3H + CH_3 + CO$, the conclusion is drawn that the pyrolysis is unimolecular and the chain part due to an impurity. For the unimolecular reaction, the ratio of the rate constants for the pyrolysis of $CH_3CHO$ and $CD_3CDO$ would be 1.3 - 1.4, and not ~ 2.4 as from the data of ([28]) (.9).

**(.11)** Products at 550° C, 4 mm Hg:
$CO$(40 %), $H_2$(20 %), $CH_4$(10 %), $C_2H_6$(10 %), $C_nH_{2n}$(20 %)
at 550°, 200 mm Hg:
$CO$(50 %), $H_2$(5 %), $CH_4$(10 %), $C_2H_6$(25 %), $C_nH_{2n}$(10 %);
iodine-catalyzed reaction, $CO + C_2H_6$. Large relative concentrations of $C_3H_6$ have a catalytic effect (see half-lives for $A_o$ = 50 mm, $C_3H_6$ = 50 and 200 mm.) Para-ortho hydrogen method shows presence of radicals ([20a]). Catalysis by iodine ([1a]) produced by decomposition of $(CH_3)_2CHI$; proposed mechanism $A + I_2 \longrightarrow A^*$ ($k$); $A^* + A \longrightarrow$ inactive products ($k'$); $A^* \longrightarrow$ final products ($k''$); $b = k'/k''$; other interpretation see ([26a]). Further literature ([12a])([29a]). **(.12)** Products are $CO$(50 %), $CH_4$(15 %), $C_2H_6 + H_2$(15 %), $C_2H_4$(10 %), $C_4H_8$(10 %). Order between 1 and 2. Tentative rate constants at 530° C, 100 mm Hg: for $kA^2$, $k = 1.7 \times 10^{-5}$, and for $kA$, $k = 4.3 \times 10^{-5}$. Composite reaction, with several independent quasi-unimolecular processes and a superposed bimolecular one. **(.13)** $CH_2{:}CO$ decomposes further (at a 1.5-order rate ([40])) to $CO$, $H_2$, C. Influence of surface/volume ratio is small. NO is said to inhibit at low and to catalyze at high concentrations. Ratio of half-lives at 60 and 75 % completion suggests an order between 1.5 and 2 ([42]). At 460° C, the reaction shows an induction period ([1]). At 800° C and ~ 1 mm Hg, $CH_3$ radicals are found ([23]). At 400° C, introduction of $CH_3$ radicals from $Hg(CH_3)_2$ produced $(CH_3COCH_2)_2$ and no $CH_2{:}CO$ ([25]).
Suggested chain mechanism ([22]):

$$A \longrightarrow 2\ CH_3 + CO$$
$$CH_3 + A \longrightarrow CH_4 + CH_3COCH_2$$
$$(\longrightarrow CH_3 + CH_2{:}CO)$$
$$CH_3 + CH_3COCH_2 \longrightarrow C_2H_5COCH_3$$

**(.14)** Essentially homogeneous. First order at higher pressures. Rate falls sharply below 400 mm; maintained by $H_2$ but not by $N_2$, CO, or He. Apparent chain length 17,

temperature-dependent. HCHO decomposes further to $H_2$ + CO. Free radicals detected by mirror technique ([23]). Increase of the surface/volume ratio retards the rate ([21]). Sensitized by radicals from photolyzing acetone ([16]) and by biacetyl ([15]); in the latter case, partly suppressed by NO. Retarded by NO ([33, 15, 19]) and by $C_3H_6$ ([24]). The inhibition is interrupted to indicate two processes, a decomposition by molecular rearrangement (not inhibited by NO) and a decomposition into radicals (with $E \sim 80$) with a chain of $E \sim 12$, chain length $\sim 400$. **(.15)** Composition of products ([36]): $CH_4$(50 %), CO(30 %), $H_2$(9 %), $C_2H_6$(5 %), $C_2H_4$(3 %), $CO_2$ (?). $CH_3CHO$ and HCHO are found as intermediate products. The $E$ value of ([34]) (55 kcal at $\infty$ pressure, 54 at 650 mm, from quarter-lives) is in line with the series 58, 55, 49, for $CH_3OCH_3$, $CH_3OC_2H_5$, $CH_3OC_3H_7$, and with the series 58, 55, 53, for $CH_3OCH_3$, $CH_3OC_2H_5$, $C_2H_5OC_2H_5$. For the uncatalyzed reaction in iodine-free $CH_3OC_2H_5$ ([36]) calculate both a first-order $k$ in $CH_3OC_2H_5$ and a second-order $k$ in $CH_3CHO$, with the reaction assumed to proceed over $CH_3OC_2H_5 \longrightarrow CH_4 + CH_3CHO$ followed by $CH_3CHO \longrightarrow CH_4 + CO$, both rates treated as comparable at 487° and 509° C. The second-order $k$ are omitted as the derived rates compare only fairly with the directly determined rates of decomposition of $CH_3CHO$ (see .2, .3). For the $C_2H_5I$ — catalyzed reaction ([36]) give also a first-order $k$ in $CH_3CHO$ (omitted). In the work of ([2]), $I_2$ is supplied by decomposing $(CH_3)_2CHI$. Previous data of ([6]) showing obviously erroneous higher rates for the uncatalyzed as compared with the iodine-catalyzed reaction ([2]) are omitted, as these data have been subsequently ([33]) recognized to have been vitiated by traces of iodine. Both the catalyzed and uncatalyzed reactions are essentially homogeneous; first-order $k$ first rise, then fall somewhat with the progress of the reaction. Half-lives are independent of the pressure even at low pressures if reaction products or $H_2$ are present. Catalysis by $I_2$ is proportional to its amount ([2]). From the inhibition by 1 mm NO ([33]), the chain length at 560° C under 400 mm is 7.3. **(.16)** Essentially homogeneous. Decomposition into $C_3H_6 + H_2$ + CO to the extent of about 10 % of the total reaction. Rate constants from half-lives. Inhibition by NO suggests radicals **(.17)** Essentially homogeneous. Rate is proportional to the amount of $I_2$. The HCHO formed decomposes further into CO + $H_2$. **(.18)** First order by the approximate pressure independence of fractional time. Free radicals produced in the reaction. However, NO is without effect. **(.19)** Composition of products $CH_4$($\sim$ 65 %), CO($\sim$ 20 %), $C_nH_{2n}$($\sim$ 15 %). Roughly first-order from half-lives. Rate constants from half-lives. **(.20)** The iodine-catalyz-

ed reaction seems to follow the simple stoichiometric equation, with a final pressure increase of 100 %. (.21) In the presence of excess $C_6H_5CH_3$ as carrier gas, a mixture of $CH_4$ and $C_2H_6$ is produced, with 50 - 80 % $C_2H_6$, and the proportion of $CH_4$ increasing with the excess of $C_6H_5CH_3$. The final pressure increase is 2.88. Without $C_6H_5CH_3$, the rate is about 50 % greater. The initial step is $A \rightarrow 2(CH_3)_3CO$, followed by $(CH_3)_3CO \rightarrow CH_3COCH_3 + CH_3$, followed, in the absence of carrier gas, by $CH_3 + CH_3 \rightarrow C_2H_6$, and in the presence of $C_6H_5CH_3$, by $CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2$. The activation energy $E$ = 34 is identified with the bond dissociation energy $(CH_3)_3CO - OC(CH_3)_3$.

(.22) First-order $k$ falls after 30 % decomposition. Activation entropy = 14.5. Assumed 3 mole product per 1 mole A. Mechanism suggested: $A \rightarrow 2\ (CH_3)_3CO$

$$(CH_3)_3CO \rightarrow (CH_3)_2CO + CH_3$$
$$CH_3 + (CH_3)_2CO \rightarrow CH_3COC_2H_5$$
$$CH_3 + CH_3 \rightarrow C_2H_6$$

involves the same initial steps as the mechanism of ([34a]) (.21) for the high-temperature pyrolysis of A.

(.23) Assumed 3 moles product per 1 mole A, valid only at low pressures; 1 mole ketone yielded per mole A. At higher pressures, accompanying higher-order reaction probable.

## LITERATURE

(1) A.O.Allen, *ACS* 1936, **58**, 1052. (1a) S.Bairstow, C.N.Hinshelwood, *PRS*[A] 1933, **142**, 77. (2) P.A.K.Clusius, *CSL* 1930, 2607. (3) C.J.M.Fletcher, *PRS*[A] 1934, **146**, 357. (4) C.J.M.Fletcher, C.N.Hinshelwood, *PRS*[A] 1933, **141**, 41. (5) C. J. Fletcher, G. K. Rollefson, *ACS* 1936, **58**, 2135. (6) J. V. S. Glass, F. N. Hinshelwood, *CSL* **1929**, 1804. (7) J. V. S. Glass, C. N. Hinshelwood, *CSL* **1929**, 1814. (8) C. N. Hinshelwood, P. J. Askey, *PRS*[A] 1927, **116**, 163. (9) C. N. Hinshelwood, P. J. Askey, *PRS*[A] *1927*, **115**, 215. (10) C. N. Hinshelwood, C. J. M. Fletcher, *TFS* 1934, **30**, 614. (11) C.N.Hinshelwood, W.K.Hutchinson, *PRS*[A] 1926, **111**, 380. (12) C.N.Hinshelwood, W.K.Hutchinson, *PRS*[A] 1926, **111**, 245. (12a) C.N.Hinshelwood, H.W.Thompson, *PRS*[A] 1926, **113**, 221. (13) J.R.Huffman, *ACS* 1936, **58**, 1815. (14) L.Kassel, *JCP* 1930, **34**, 1165. (15) C.N.Klute, W.D.Walters, *ACS* 1945, **67**, 550. (16) J.A.Leermakers, *ACS* 1934, **56**, 1899. (17) M.Letort, *JCC* 1937, **34**, 265, 355. (18) M.Letort, *JCC* 1937, **34**, 428. (19) J.W.Mitchell, C.N.Hinshelwood, *PRS*[A] 1937, **159**, 32. (20) J. C. Morris, *ACS* 1944, **66**, 584. (20a) F. Patat, H. Sachsse, *ZPC*[B] 1935, **31**, 105. (21) R.N.Pease, *ACS* 1937, **59**, 425. (21a) J.R.Raley, F.F.Rust, W.E.Vaughan, *ACS* 1948, **70**, 88. (22) F.O.Rice, K.Herzfeld, *ACS* 1934, **56**, 284. (23) F.O.Rice, W.R.Johnston, *ACS* 1934, **56**, 214. (24) F.O.Rice, O.K.Polly, *JCP* 1938, **6**, 273. (25) F.O.Rice, E.L.Rodowskas, W.R.Lewis, *ACS* 1934, **56**, 2497. (26) F.O.Rice, R.E.Vollrath, *PNA* 1929, **15**, 702. (26a) G.K.Rollefson, R.F.Faull, *ACS* 1937, **59**, 625. (27) Seddon, M.Travers, *PRS*[A] 1936, **156**, 234. (28) R.E.Smith, *TFS* 1939, **35**, 1328. (28a) J.R.E.Smith, C.N.Hinshelwood, *PRS*[A] 1942, **180**, 237. (29) J.R.E.Smith, C.N.Hinshelwood, *PRS*[A] 1944, **183**, 33. (29a) L.A.K.Staveley, C.N.Hinshelwood, *CSL* **1936**, 812. (30) L.A.K.Staveley, C.N.Hinshelwood, *PRS*[A] 1937, **159**, 192. (31) L. A. K. Staveley, C. N. Hinshelwood, *PRS*[A] 1937, **159**, 200. (32) L.A.K.Staveley, C.N.Hinshelwood, *CSL* **1937**, 1568. (33) L. A. K. Staveley, C. N. Hinshelwood, *PRS*[A] 1937, **159**, 198. (34) E.W.R.Steacie, *JCP* 1933, **1**, 618. (34a) M. Szwarc, J. S. Roberts, *JCP* (in press) 1950. (35) H. W. Thompson, J.J.Frewing, *CSL* **1935**, 1443. (36) W.Ure, J.T.Young, *JCP* 1933, **37**, 1169, 1183. (37) F.H.Verhoek, *TFS* 1935, **31**, 1527.

## LITERATURE (*continued*)

(38) F.H.Verhoek, *TFS* 1935, **31**, 1533. (39) S.N.Wang, C.A.Winkler, *CJR*[B] 1943, **21**, 97. (40) A.T.Williamson, *ACS* 1934, **56**, 2216. (40a) C.A.Winkler, C.J.M.Fletcher, C.N.Hinshelwood, *PRS*[A] 1934, **146**, 345. (41) C.A.Winkler, C.N.Hinshelwood, *PRS*[A] 1935, **149**, 355. (42) C.A.Winkler, C.N.Hinshelwood, *PRS*[A] 1935, **149**, 340.



942151 O—51——36

# PYROLYSIS

## Aromatic C, H, O, compounds

*Gas phase*

Amounts are in mm Hg.

Rates are in mm Hg/sec.

**Homogeneous Reactions**

**571.442.**

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CHO \rightarrow C_6H_6 + CO$ | p | 14 | | | +p | $kA$ | 550 | 2.3 | -3 | | * | ([1]) |
| | | | 58 | | | | | " | 4.6 | -3 | | | |
| | | | 100 - 300 | | | | | " | 6.2 | -3 | | | |
| | | | 23 | NO | 5 | +p | $kA$ | 550 | 6.0 | -4 | 63 | * | " |
| | | | 144 | | | | | " | 1.9 | -3 | 58 | | |
| | | | 250 | | | | | " | 2.8 | -3 | 57 | | |
| | | | | | | | | | | | (520 - 590°) | | |
| .2 | $p$ - $CH_3C_6H_4CHO \rightarrow C_6H_5CH_3 + CO$ | p | 25 | | | +p | $kA$ | 550 | 2.8 | -3 | | * | ([2]) |
| | | | 100 - 200 | | | | | " | 3.9 | -3 | | | |
| | | | 20 | NO | 5 | " | " | " | 5.9 | -4 | | | |
| | | | 81 | | | | | " | 1.2 | -3 | | | |
| | | | 218 | | | | | " | 2.4 | -3 | | | |
| .3 | $p$ - $ClC_6H_4CHO \rightarrow C_6H_5Cl + CO$ | p | 18 | | | +p | $kA$ | 550 | 2.6 | -3 | | | |
| | | | 63 | | | | | " | 4.9 | -3 | | | |
| | | | 110 - 175 | | | | | " | 8.3 | -3 | | | |

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Rate measured | Defined rate law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $p$ - $ClC_6H_4CHO \rightarrow C_6H_5Cl + CO$ *(continued)* | | 21<br>64<br>166 | NO | 5 | +p | $k$ A | 550<br>"<br>" | 7.0<br>1.1<br>2.3 | -4<br>-3<br>-3 | 58<br>(520 - 580°) | | |

## COMMENTS

(.1) Product composition CO (~ 50 %), $C_6H_6$ (~ 35 %), $H_2$ (~ 15 %), liquid ($C_6H_5.C_6H_5$). First-order $k$ calculated from half-lives but the actual order is higher. Order of inhibited reaction between 1 and 2. The inhibited reaction is interpreted as molecular rearrangement. (.2) Some amount of $(CH_3C_6H_4)_2 + H_2$ also formed. Order higher than 1. (.3) Some amount of $(ClC_6H_4)_2 + H_2$ also formed. Order higher than 1.

## LITERATURE

(1) R. E. Smith, C. N. Hinshelwood, *PRS*[A] 1940, **175**, 131.

(2) R. E. Smith, *TFS* 1940, **36**, 983.

# PYROLYSIS

## Heterocyclic C, H, O Compounds

*Gas phase*

Rates are in "unit of amount" per sec.

| No. | Reaction | Method | Unit of amount | Amount of reactant | Defined mass action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_4H_8O \rightarrow C_2H_4$, CO, $CH_4$ | p | mmHg | 200 | $kA^{3/2}$ | | (0.5) | | | | | | * | ([4]) |
| | Furane ($H_2$, $C_2H_6$, $C_3H_8$...) | | | | | 529.5 | 4020 | | | | | | | |
| | | | | | | 550.5 | 1740 | | | | | | | |
| | | | | | | 596.0 | 840 | | | 53 | 1.2 | 12 | | |
| .2 | $C_4H_8O_2 \rightarrow$ 2 CO + $H_2$ + $C_2H_6$ (a) | p | atm | 70 - 700 mmHg | $kA^{3/2}$ | 450 | | 8.9 | -5 | | | | * | ([1]) |
| | $C_4H_8O_2 \rightarrow$ 2 CO + 2 $CH_4$ (b) | | | | | 498 | | 1.1 | -3 | | | | ([3]) | ([2]) |
| | 1,4 - Dioxane | | | | | 535 | | 6.5 | -3 | 58.5 | 4.5 | 13 | | |

## COMMENTS

(.1) Products $C_2H_4$ ~ 22 %, $C_3H_8$ up to 8 %. Slight induction period. Intermediate products $CH_3CHO$ and HCHO. No inhibition by NO or $C_3H_6$. (.2) Reaction (b) to the extent of 6 - 8 % $CH_4$. Strong inhibition by NO, maximum with 1 - 3 % NO. Larger amounts of NO promote a first - order reaction with $E$ = 71 kcal, $A \sim 10^{14}$ ([3]); 4.0 - 4.5 moles dioxane consume 1 mole NO ([3]). $CH_3$ radicals from azomethane have little effect on the decomposition; para - $H_2$ method shows slight effect ([3]). Reaction catalyzed by HCl ([1]).

## LITERATURE

([1]) R.P. Bell, R.LeG. Burnett, *TFS* 1939, **35**, 474.
([2]) T. Gross, H. Suess, *MHC* 1936, **68** 207.
([3]) L. Kuchler, T.D. Lambert, *ZPC*$^B$ 1937, **37**, 285.
([4]) C.H. Klute, W.D. Walters, *ACS* 1946, **68**, 506.

# PYROLYSIS

## Aliphatic C, H, N compounds

*Gas phase*

**Homogeneous reactions**
**571.451.**

All rates are in "unit of amount" per sec.

| No. | Reaction | Method | Unit of Amount | Amount of reactant | Addend | Rate measured | Defined mass action law | Temperature | Fraction time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | (a) | | | (a) | | | | | | | |
| .1 | $CH_3NH_2 \rightarrow HCN + 2H_2$ (a) | $p$ | mm Hg | 30- | | $+p$ | $k$ A | 593 | | 1.0 | -3 | | | | | | ([3]) |
| | | | | 250 | | | | 618 | | 2.3 | -3 | | | | | | |
| | $CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$ (b) | | | | | | | 640 | | 5.0 | -3 | 58 | 3.3 | 11 | * | * | " |
| | | | | | | | | 667 | | 1.5 | -2 | | | | | | |
| .2 | $2(CH_3)_2NH \rightarrow (CH_3)_3N + CH_3NH_2$ | | | | | | | 420 | | | | | | | * | * | ([2]) |
| | | | | | | | | -440 | | | | | | | | | |
| | $CH_3NH_2 \rightarrow CH_4 + CH_3N{:}CH_2$ | | | | | | | | | | | | | | | | |
| .3 | $(CH_3)_3N \rightarrow CH_4 + C_2H_5N^{\cdot}$ | anal | M/l | 0.012 | | +L | $k$ A | 380 | | 4.0 | -6 | | | | | | ([2]) |
| | | | | | | | | 400 | | 1.9 | -5 | | | | | | |
| | $(H_2,\ C_2H_6)$ | | | | | | | 420 | | 5.9 | -5 | | | | * | * | |
| | | | | | | | | 430 | | 1.7 | -4 | | | | | | |
| | | | | mm Hg | | | | | | | | | | | | | |
| .4 | $2C_2H_5NH_2 \rightarrow C_2H_5NHNHC_2H_5 + H_2$ | $p$ | " | 224 | | -A | $k$ $A^2$ | 482 | | 3.0 | -3 | | | | | | ([12]) |
| | | | | 33 | | | | 490 | | 2.2 | -2 | 38 | | | * | * | |
| | | | | | | | | | (0.25) | | | | | | | | |
| .5 | $(C_2H_5)_2NH \rightarrow NH_3,\ C_nH_{2n},\ H_2,\ CH_4,\ C_2H_6,\ N_2$ | " | mm Hg | 44 | | +p | | 510 | 228 | | | | | | | | ([13]) |
| | | | | 419 | | | | " | 90 | | | | | | | | |
| | | | | 37 | | | | 520 | 138 | | | | | | | | |
| | | | | 437 | | | | " | 58 | | | | | | | | |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Rate measured | Defined mass action law | Temperature | Fraction time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $(C_2H_5)_2NH \rightarrow NH_3, C_nH_{2n}, H_2, CH_4, C_2H_6, N_2$ (*continued*) | $p$ | mm Hg | 43 | | +p | | 530 | 87 | | | | | | | | |
| | | | | 452 | | | | " | 41 | | | | | | | | |
| | | | | 41 | | | | 540 | 72 | | | 49 | | | * | * | ([13]) |
| | | | | 358 | | | | " | 32 | | | | | | | | |
| .6 | $C_3H_7NH_2 \rightarrow$ ? | $p$ | " | 1.40 | | +p | $k$ A | 500 | | 1.55 | -4 | | | | | | ([10]) |
| | | | | 34.7 | | | | " | | 3.48 | -4 | | | | | | |
| | | | | 1.40 | | | | 520 | | 3.58 | -4 | | | | | | |
| | | | | 34.3 | | | | " | | 7.96 | -4 | | | | | | |
| | | | | 3.14 | | | | 540 | | 3.68 | -4 | | | | * | | |
| | | | | 36.8 | | | | " | | 1.72 | -3 | | | | | | |
| .7 | $n\text{-}C_4H_9NH_2 \rightarrow C_2H_6, H_2, CH_4, NH_3, C_2H_4, C_2H_2$, liquid (30% N) | $p$ (anal) | " | 45 | | +p | $k$ A | 510 | | 2.82 | -4 | | | | | | ([1]) |
| | | | | 217 | | | | " | | 4.03 | -4 | | | | | | |
| | | | | 41 | | | | 520 | | 5.58 | -4 | | | | | | |
| | | | | 220 | | | | " | | 7.66 | -4 | | | | | | |
| | | | | 35 | | | | 530 | | 1.55 | -4 | | | | * | | |
| | | | | 240 | | | | " | | 1.66 | -3 | | | | | | |
| | | | | | | | | | (0.2) | | | | | | | | |
| .8 | $CH_2N_2 \rightarrow N_2 + 1/2\ C_2H_4$ | " | " | 45 | | +p | $k\ A^2$ | 135 | $3.8 \times 10^4$ | | | | | | | | ([11]) |
| | | | | 200 | | | | " | $9.4 \times 10^3$ | | | | | | | | |
| | | | | 45 | | | | 162 | $1.4 \times 10^3$ | | | | | | * | | |
| | | | | 155 | | | | " | $3.6 \times 10^2$ | | | | | | | | |
| | | | | 50 | | | | 217 | 12 | | | | | | | | |
| .9 | $CH_3N{:}NCH_3 \rightarrow N_2, CH_4, C_2H_6, C_2H_4, H_2$, liquid | $p$ | " | 129 | | +p | $k$ A | 292 | | 1.0 | -4 | | | | | | |
| | | | | 191 | | | | 316 | | 7.6 | -4 | | | | | | |
| | | | | 119 | | | | 336 | | 3.5 | -3 | 52.5 | 3.5 | 16 | * | * | |

| No. | Reaction | Method | Unit of amount | Amount of reactant | Addend | Rate measured | Defined mass action law | Temperature | Fraction time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Mechanism | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .9 | $CH_3N{:}NCH_3 \rightarrow N_2, CH_4, C_2H_6, C_2H_4, H_2$, liquid (*continued*) | anal | mm Hg | 129 | | −A | *k* A | 292 | | 1.6 | −4 | | | | | | |
| | | | | 191 | | | | 316 | | 1.1 | −3 | | | | | | |
| | | | | 119 | | | | 336 | | 4.9 | −3 | | | | | | |
| | | *p* | | 248 | | +p | " | 290 | | 1.2 | −4 | | | | | | ([9]) |
| | | | | 100 | | | | 11 | | 9.8 | −5 | | | | | | |
| | | | | 12 | | | | 11 | | 4.6 | −5 | | | | | | |
| | | " | | 181 | | " | | 310 | | 4.7 | −4 | | | | | | |
| | | | | 66 | | " | | " | | 3.2 | −4 | 50.2 | 8 | 15 | * | | " |
| | | | | 0.4 | | | | " | | 2.0 | −4 | (47.7) | | | | | |
| .10 | $CH_3N{:}NCH_3 \rightarrow N_2$ .... | anal | mm Hg | 100–170 | NO 200–340 | +L, −A | *k* A | 295 | | 2.0 | −4 | | | | | | ([4]) |
| | | | | | | | | 320 | | 1.1 | −3 | | | | | | |
| | | | | | | | | 331 | | 2.4 | −4 | 52.5 | | | * | * | ([4]) |
| | | | | | | | | 342 | | 3.7 | −4 | | | | | | |

## COMMENTS

(.1) Reaction (a) is homogeneous; reaction (b), heterogeneous, is treated as a side reaction. *Mechanism:* $A \rightarrow CH_3 + NH_2$; $CH_3 + A \rightarrow CH_4 + CH_3NH^{\cdot} \rightarrow CH_4 + CH_2{:}NH + H$; $NH_2 + A \rightarrow NH_3 + CH_3NH^{\cdot} \rightarrow NH_3 + CH_2{:}NH + H$; $H + A \rightarrow H_2 + CH_3NH \rightarrow H_2 + CH_2{:}NH + H$; $CH_2{:}NH \rightarrow HCN + H_2$. (.2) No rate data. (.3) Packing increases the rate; addition of He increases it slightly. *Mechanism:* $A \rightarrow CH_3 + (CH_3)_2N$; $CH_3 + A \rightarrow CH_4 + CH_2N(CH_3)_2$; $CH_2N(CH_3)_2 \rightarrow CH_3 + CH_3N{:}CH_2$. (.4) Final pressure increase is 125 - 130%. (.5) Selected points (extreme $A_o$). Proof of homogeneity given. (.6) Selected points. Initial rates of pressure increase. Sevenfold increase of pressure is without effect at 200 mm but the rate decreases by about 40 % below 4 mm Hg. (.7) Steady decrease of $k$ during one run. Initial rates decrease with pressure decrease and level off at low pressures. Products taken in a flow system at 950° with a contact time of 0.1 sec : $C_2H_6$ (37), $H_2$ (22), $CH_4$ (17), $NH_3$ (13), $C_2H_4$ (8), $C_2H_2$ (3 %). Products from runs at 500°C for one hour similar. (.8) Proof of homogeneity given. Products at 187°C: $N_2$ (69), $C_2H_4$ (29), $C_nH_{2n+2}$ (as $CH_4$) (24 %). Rate constants calculated from 0.1 times. (.9) Representative data from ([8]) and ([9]). Further literature references, ([10]) to ([13]). According to ([10]), products at 340°C are $0.7N_2$, 0.3 $C_2H_6$, 0.4 - 0.7 $CH_4$ (depending on extent of decomposition), 0.3 liquid; extrapolated to zero decomposition, 0.5 $N_2$, 0.5 liquid. Mean composition of liquid H/N ~ 5, C/N ~ 2 ([8]). Final pressure increase 195 % ([8]). Analyses of ([8]) are in general agreement with this but give less $C_2H_6$ (~ 0.1), and more $CH_4$. Liquid is mainly $(CH_3)_2NN(CH_3)_2$. *Mechanism:* $A \rightarrow N_2 + 2CH_3$; $2CH_3 + A \rightarrow (CH_3)_2NN(CH_3)_2$ ([8]). (.10) Only very slight increase of pressure; hardly any hydrocarbons formed. NO/A = 2:1 reduces the rate to about one half. Product is mainly $N_2$ in 1:1 ratio to A decomposed. Average number of NO reacting per one A is ~ 2 (1.4 - 2.2). Some $CO_2$ formed, attributed to reaction of excess NO with HCHNOH. *Mechanism:* $A \rightarrow N_2 + 2CH_3$; $CH_3 + NO \rightarrow HCHNOH$ ([14]).

## LITERATURE

(1) H.C.Beachel, H.A.Taylor, *JCP* 1942, 10, 106. (2) A.G.Carter, P.V.Bosanquet, C.G.Silcocks, M.W.Travers, A.F.Wilshire, *CSL* 1939, 495. (3) H.J.Emeleus, L.J.Jolly, *CSL* 1935, 929. (4) F.P.Jahn, H.A.Taylor, *JCP* 1939, 7, 474. (5) (L. Kassel, *JPC* 1928, 32, 225, 1065). (6) (Ramsperger, *ACS* 1927, 49, 912, 1395). (7) Riblett, Rubin, *ACS* 1937, 59, 1537. (8) (Rice, Ramsperger, *ACS* 1928, 50, 617). (9) O.K.Rice, D.V. Sickman, *JCP* 1936, 4, 239, 243, 608. (10) D.V.Sickman, O.K.Rice, *ACS* 1935, 57, 22. (H.A.Taylor, Achilles, *JCP* 1931, 35, 2658).

(11) E. W. R. Steacie, *JPC* 1931, 35, 1493. (12) H. A. Taylor, J. G. Ditman, *JCP* 1936, 4, 212. (13) H. A. Taylor, C. R. Herman, *JPC* 1935, 39, 803. (14) H. A. Taylor, F. P. Jahn, *JCP* 1939, 7, 470.

## Aromatic nitro compounds

Amounts are in mm Hg.
Rates in mm Hg per sec.

| No. | Reaction | Amount of reactant | Rate measured | Temperature | Half-time | *E* |
|---|---|---|---|---|---|---|
| .1 | $C_6H_5NO_2 \rightarrow C_6H_6$(~ 40 %), NO(~ 30 %), CO(~ 15 %) + $N_2$, $NO_2$, $H_2$, unsatd. | 20 | $+\Delta p$ | 500 | 190 | |
| | | 85 | | " | 150 | |
| | | ~ 15 | | 455 | 1420 | |
| | | | | 470 | 820 | |
| | | | | 485 | 360 | 51 |
| .2 | $m$ - $NO_2C_6H_4NO_2 \rightarrow$ CO( ~ 45 %), NO(~ 30 %) + $C_6H_5$(?) | ~ 15 | | 440 | 875 | |
| | | | | 470 | 235 | |
| | | | | 500 | 70 | 48 |

### COMMENTS

**(.1)** Order between 1 and 2. Half-time is increased by packing.

### LITERATURE

R. E. Smith, *TFS* 1940, **36**, 983.

# PYROLYSIS

## Aliphatic halogen compounds

*Gas phase*

**Homogeneous Reactions**
**571.471.**

Rate measured + $\Delta p$

Amounts are in mm Hg.
Rates are in mm Hg per sec.

| No. | Reaction | Method | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | Fractional time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CCl_3CHO \rightarrow CO + CHCl_3$ ($\rightarrow CO + HCl, C_2Cl_6, C...$) | $p$ | | | | | | (0.5) | | | |
| | | | 120 | | | $k$ A | 400 | 1200 | | | |
| | | | | | | | 430 | 270 | | | |
| | | | | | | | 466 | 60 | | | |
| | | | 225 | | | " | 400 | 1100 | 6.0 | -4 | |
| | | | | | | | 430 | 220 | 2.5 | -3 | |
| | | | | | | | 466 | 50 | 1.26 | -2 | 49 |
| | | | 50 - 300 | X = $(CH_3)_2CHI$ | 5 | $k\,AX^{1/2}$ | 353 | 750 | | | |
| | | | | | | | 380 | 130 | | | |
| | | | | | | | 412 | 50 | | | 39 |
| | | | | NO | 50 | $k$ AX | 401 | 350 | | | |
| | | | | | 90 | | 356 | 1200 | | | |
| | | | | | " | | 401 | 180 | | | |
| | | | | | " | | 421 | 75 | | | |
| | | | | | 310 | | 401 | 55 | | | 37 |

### COMMENTS

Without addend, the reaction (from the half-lives) is first-order above 20 mm Hg. Order in $(CH_3)_2CHI$ is approximately 0.5 or more complex; the catalytic effect of $(CH_3)_2CHI$ is due to $I_2$, formed by $(CH_3)_2CHI \rightarrow C_3H_6 + I_2$.

### LITERATURE

F. H. Verhoek, C. N. Hinshelwood, *PRS*[A] 1934, 146, 334. F. H. Verhoek, *TFS* 1935, 31, 1521.

# DECOMPOSITION

## Alicyclic ring ⟶ Unsaturated compounds

*Gas phase*

Rate measured $+\Delta p$

Mass action is in M/l. Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_8H_{10}O \longrightarrow cyclo - C_5H_6 + CH_2{:}CHO$ | A = 15 - 64 mm; | $kA$ | 192 | 3.5 | -4 | | | | * |
| | endomethylene - 2,5 - tetrahydrobenzaldehyde | L = 45 - 363 mm; | | 206 | 1.0 | -3 | | | | |
| | | B = 42 - 328 mm; | | 215 | 2.0 | -3 | | | | |
| | | | | 230 | 5.3 | -3 | | | | |
| | | | | 242 | 1.2 | -2 | 33.6 | 2.2 | 9 | |

## COMMENTS

Initial $k$. Reverse reaction, see 681.441.

## LITERATURE

G. B. Kistiakowsky, J. R. Lacher, *ACS* 1936, 58,123.



942151 O—51——37

# ASSOCIATION

## Aldehyde + Anhydride → Dicarboxylate

*Gas phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Defined mass-action law | Temperature | $E$ | $A = A^{\circ} \times 10^{n}$ $A^{\circ}$ | $n$ |
|---|---|---|---|---|---|---|
| .1 | $C_6H_5CHO + (CH_3CO)_2O \rightarrow (CH_3COO)_2CHC_6H_5$ | $k$ AB | 200 - 300 | 22.9 | 5.8 | 7 |

## COMMENTS

From the rate of the reverse reaction (see 511.443.) and the equilibrium constant, assumed to be the same in gas as in liquid phase.

## LITERATURE

N. A. D. Parlee, J. C. Arnell, C. C. Coffin, *CJR*[B] 1940, 18, 223.

# ADDITION

## Aldehyde + $H_2O$ → Hydrate

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Defined mass-action law | Temperature | $k^o = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CHO + H_2O \rightarrow CH_3CH(OH)_2$ | $H_2O$ | ~ 0.4 | | $k\,A = (k_o[H_2O] + k_H[H^+] + k_{OH}[OH^-])A$ | | | |
| | | | | | | 0 | $k_o$ 2.96 | -5 |
| | | | | | | " | $k_H$ 1.15 | +2 |
| | | | | | | " | $k_{OH}$ 9.6 | +3 |
| | | | | X = | $k'A = (k + (k_{HX} + k_X/r)[HX])A$ | | | |
| | | | | $m$-$NO_2C_6H_4COO^-$ | $r = [HX]/[X^-]$ | 0 | $k_{HX}$ 3.8 | -3 |
| | | | | | | " | $k_X$ 6.1 | -1 |
| | | | | $p$-$NO_2C_6H_4COO^-$ | | 0 | $k_{HX}$ 6.9 | -3 |
| | | | | | | " | $k_X$ 1.34 | -1 |
| | | | | $CH_3COO^-$ | | 0 | $k_{HX}$ 1.23 | -1 |
| | | | | | | " | $k_X$ 1.65 | -2 |
| | | | | $C_6H_5COO^-$ | | 0 | $k_{HX}$ 1.25 | -1 |
| | | | | | | " | $k_X$ 1.34 | -2 |

## COMMENTS

Values of $k_{HX}$ and $k_X$ obtained graphically by plotting $k_{HX} + k_X/r$ against $1/r$ (where $r = [HX]/[X]$), after correction of the rates for $k\,A = (k_o[H_2O] + k_H[H^+] + k_{OH}[OH^-])A$. Data converted to ln and sec. Acid catalysis is attributed to the rate determining step $A + H_2O + HX \rightarrow CH_3CH(OH)(OH_2^+) + X^-$, base catalysis to $A + H_2O + X^- \rightarrow CH_3CH(OH)O^- + HX$. Reverse reaction, see 612.410.

## LITERATURE

R. P. Bell, B. de B. Darwent, *TFS* 1950, 46, 34.

# ADDITION

## HCN to carbonyl

*Liquid phase*

Reaction type **ArCHO + HCN → ArCH(OH)CN**

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5CHO + HCN$ | $C_2H_5OH$ | $C_5H_5N{\cdot}C_6H_5COOH$ | 0.01 | $k$AB | 20 | 1.96 | −8 |
| .2 | $p\text{-}CH_3C_6H_4CHO + HCN$ | $C_2H_5OH$ | $C_5H_5N{\cdot}C_6H_5COOH$ | 0.01 | $k$AB | 20 | 9.8 | −9 |
| .3 | $p\text{-}C_2H_5C_6H_4CHO + HCN$ | $C_2H_5OH$ | $C_5H_5N{\cdot}C_6H_5COOH$ | 0.01 | $k$AB | 20 | 1.01 | −8 |
| .4 | $p\text{-}(CH_3)_2CHC_6H_4CHO + HCN$ | $C_2H_5OH$ | $C_5H_5N{\cdot}C_6H_5COOH$ | 0.01 | $k$AB | 20 | 8.5 | −9 |
| .5 | $p\text{-}(CH_3)_3CC_6H_4CHO + HCN$ | $C_2H_5OH$ | $C_5H_5N{\cdot}C_6H_5COOH$ | 0.01 | $k$AB | 20 | 9.1 | −9 |

### COMMENTS

Reverse reaction, see 512.415.

### LITERATURE

J. W. Baker, M. L. Hemming, *CSL* **1942**, 191.

## Hydrogenation of multiple bond

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactants | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .1 | $C_2H_2 + H_2 \rightarrow C_2H_4$ | A/B = 1/8; 1/16; 1/24 | $k$AB | 495 | 1.3 | -1 | | | | * | ([2]) |
| | | | | 505 | 2.3 | -1 | | | | | |
| | | | | 515 | 3.2 | -1 | | | | | |
| | | | | 525 | 4.6 | -1 | | | | | |
| | | | | 535 | 6.4 | -1 | 42 | | | | |
| .2 | $C_2H_4 + H_2 \rightarrow C_2H_6$ | A = 195 (mm Hg) B = 573 | $k$AB | 475 | 4.7 | -3 | | | | * | ([2]) |
| | | 196 575 | | 500 | 1.14 | -2 | | | | | |
| | | 198 580 | | 524 | 2.79 | -2 | | | | | |
| | | 191 562 | | 552 | 7.76 | -2 | 43.1 | 1.24 | 6 | | |
| | | 100 294 | | 548 | 6.92 | -2 | | | | * | " |
| | | 48 141 | | 550 | 8.20 | -2 | | | | | |
| | | A/B = 1/2; 1/1 | | 549 | 5.6 | -2 | | | | * | " |

## COMMENTS

(.1) Manometric measurements. $k$ from initial rates by extrapolation to zero time, making allowance for polymerization.

(.2) $k$ and $A$ converted from $mm^{-1}$ to $(M/l)^{-1}$ units. With excess of $H_2$, and up to 50 % conversion, $k$ is not appreciably affected by reverse reaction. Increase of the surface/volume ratio by a factor of > 10 doubles the rate of disappearance of $H_2$ but not of $C_2H_4$, i.e. increase of the surface consumes $H_2$ through adsorption but does not affect the rate of the reaction. Side reactions are practically absent at A/B = 1:3 but at A/B = 1:2 or 1:1, some polymerization occurs, hence $k$ is lowered. Combination of the data of $k$ with the rate constant of Marek and McCluer, *IEC* 1931, **23**, 878, for the reverse reaction (see 571.411.) gives the correct value for the equilibrium constant. Collision efficiency ~ 10 %.

## LITERATURE

(1) H.A.Taylor, A.van Hook, *JPC* 1935, **39**, 811.

(2) R.N.Pease, *ACS* 1932, **54**, 1877.

# ADDITION

## Bond Saturation

## Addition of hydrogen halide to double bond

*Gas phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Defined mass-action law | Temperature | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|
| .1 | $(C_2H_4 + HF \rightarrow C_2H_5F)$ | — | | 64.3 | | | * | ([3]) |
| .2 | $C_2H_4 + HCl \rightarrow C_2H_5Cl$ | — | | 48.4 | | | * | ([2]) |
| .3 | $C_2H_4 + HBr \rightarrow C_2H_5Br$ | — | | 39.0 | | | * | |
| .4 | $C_2H_4 + HI \rightarrow C_2H_5I$ | — | | 31.5 | | | * | |
| .5 | $(CH_3)_2C{:}CH_2 + HCl \rightarrow (CH_3)_3CCl$ | $k$AB | 88 - 260 | 28.8 ±2.4 | 1 | 8 | * | ([1]) |
| .6 | $(CH_3)_2C{:}CH_2 + HBr \rightarrow (CH_3)_3CBr$ | $k$AB | 88 - 260 | 22.5 ±1.9 | 1.6 | 7 | * | ([1]) |

## COMMENTS

**(.1) (.2) (.3) (.4)** *E* by quantum-mechanical calculation from Morse curves. For reaction (.1) *E* exceeds the energy of dissociation of the C – C bond, hence reaction (.1) cannot take place. **(.5) (.6)** Calculated from the rates of the reverse reactions (which see 521.471.) and equilibrium between 88° and 260°C. *A* converted from $(M/ml)^{-1}$ to $(M/l)^{-1}$ units. The second order is assumed.

All data are given only in the way of an order of magnitude.

## LITERATURE

(1) D.Brearly, G.B.Kistiakowsky, C.H.Stauffer, *ACS* 1936, **58**, 43; G.B.Kistiakowsky, C.H.Stauffer, *ACS* 1937, **59**, 165. (2) C.E.Sun, C.Liu, *J. Chinese Chem. Soc.* 1936, **4**, 98. (3) C.E.Sun, C.H.Sze, *ibid.* 1937, **5**, 1.

# BOND SATURATION

## Addition of halogen to Double bond

*Gas phase*

Amounts are in mm Hg.

Rates are in mm Hg per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|
| .1 | $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ | A ~ B ~ 9 | $k$ | 16 | 7.5 | -3 |
| | | | $k$ B | 16 | 3.1 | -4 |
| | | | $k$ AB | 16 | 2.5 | -5 |

## COMMENTS

The rate and the order of the reaction vary strongly with the nature of the wall surface. The above data are quoted only as an illustration of the orders of magnitude involved. For a given surface, lower temperature or higher pressure tend to lower the order of the reaction. $H_2O$ vapor accelerates the rate. Wet surface, high initial $[Br_2]$, and low temperature, favor transition from second to first order. With a high surface concentration of the initial $Br_2$, the reaction tends to zero order. Addition of $C_2H_4Br_2$ accelerates the rate.

## LITERATURE

(1) R. G. W. Norrish, *CSL* 1923, 123, 3006. (2) R. G. W. Norrish, G. G. Jones, *CSL* 1926, 129, 55. (3) F. F. Rust, W. E. Vaughan, *JOC* 1940, 5, 472; 1941, 6, 479. (4) A. Sherman, O. T. Quimby, R. O. Sutherland, *JCP* 1936, 4, 732. (5) W. E. Vaughan, F. F. Rust, *JOC* 1940, 5, 449. (6) G. Williams, *CSL* 1932, 135, 1747.

# BOND SATURATION

## Addition of $H_2O$ to C:C bond

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3)_2C{:}CH_2 + H_2O \rightarrow (CH_3)_3CHO$ | $H_2O$ | Sat | | | $k A [H^+]$ | | | | | * | (1) |
| | | | $KNO_3$, $\mu$ = 1.0, + $HNO_3$ | | 0.05 | | 25 | 6.55 | -4 | | | |
| | | | | | 0.1 | | " | 5.85 | -4 | | | |
| | | | | | 0.5 | | " | 5.94 | -4 | | | |
| | | | $\mu$ = 2.0 | | 0.1 | " | " | 9.08 | -4 | | | |
| | | | | | 0.5 | | " | 9.11 | -4 | | | |
| | | | | | 1.0 | | " | 8.32 | -4 | 23.4 (25-35°) | | |
| .2 | $(CH_3)_2C{:}CHCH_3 + H_2O \rightarrow (CH_3)_2COHC_2H_5$ | $H_2O$ | Sat | | | $k A [H^+]$ | | | | | * | (2) |
| | | | $KNO_3$, $\mu$ = 0.5, + $HNO_3$ | | 0.05 | | 25 | 2.14 | -4 | 19.2 (25-35°) | | |
| | | | | | 0.5 | | " | 2.36 | -4 | | | |
| | | | | 1.0 | 0.05 - 0.5 | | " | 3.62 | -4 | | | |
| | | | $\mu$ = 0.1, + $H_2SO_4$ | | 0.1 - 0.2 | " | " | 2.67 | -4 | | | |
| | | | $\mu$ = 0.1, + HCl | | 0.1 | " | " | 2.53 | -4 | | | |
| .3 | *trans* - $CH_3CH{:}CHCHO + H_2O \rightarrow CH_3CHOHCH_2CHO$ | $H_2O$ | | $HNO_3$ | 1.0 | $k A [H^+]$ | 25 | 6.66 | -6 | | | (4) |
| | | | | | 1.90 | | " | 6.56 | -6 | | | |
| | | | | " | 0.48 | | 35 | 1.74 | -5 | | | " |
| | | | | | 1.86 | | " | 1.70 | -5 | 18.1 | | |
| | | | | $HClO_4$ | 0.56 | " | 25 | 4.84 | -6 | | | " |
| | | | | | 0.94 | | " | 5.88 | -6 | | | |
| | | | | | 1.86 | | " | 5.96 | -6 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | *trans* - $CH_3CH{:}CHCHO + H_2O \rightarrow CH_3CHOHCH_2CHO$ *(continued)* | | | $HClO_4$ | 0.373 | $k\,A\,[H^+]$ | 35 | 1.49 | -5 | | | (4) |
| | | | | | 0.75 | | " | 1.47 | -5 | | | |
| | | | | | 1.87 | | " | 1.64 | -5 | 18.2 | | |
| .4 | $(CH_3)_2C{:}CHCHO + H_2O \rightarrow (CH_3)_2COHCH_2CHO$ | $H_2O$ | ~ 0.02 | $HNO_3$ | 0.52 | $k\,A\,[H^+]$ | 20 | 2.35 | -6 | | | (3) |
| | | | | | 1.04 | | " | 2.38 | -6 | | | |
| | | | | " | 0.52 | " | 25 | 3.74 | -6 | | | " |
| | | | | | 0.92 | | " | 3.18 | -6 | | | |
| | | | | | 1.04 | | " | 3.61 | -6 | | | |
| | | | | " | 0.52 | " | 35 | 1.07 | -5 | | | " |
| | | | | | 0.92 | | " | 1.01 | -5 | | | |
| | | | | | 1.04 | | " | 1.01 | -5 | $\Delta H_a = 19.1$ | | |

## COMMENTS

(.1) Rate approximately proportional to $[H^+]$ at constant ionic strength $\mu$. Salts of heavy metals, ~ 0.015 *M*, have a negligible effect. (.2) Selected points. Data for other acids in (2). (.3) Rate approximately proportional to $[H^+]$; $k$ calculated from original rate data.

## LITERATURE

(1) H.J. Lucas, W.F. Eberz, *ACS* 1934, **56**, 460. (2) H.J. Lucas, Y.P. Liu, *ACS* 1934, **56**, 2138. (3) H.J. Lucas, W.T. Stuart, D. Pressman, *ACS* 1944, **66**, 1818. (4) S. Winstein, H.J. Lucas, *ACS* 1937, **59**, 1461.

# BOND SATURATION

## Addition of $H_2O$ to C ⋮ C bond

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Addend | pH | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_5OC{:}CH + H_2O \rightarrow C_6H_5OCOCH_3$ | $H_2O + C_2H_5OH$ 42.7 wt % | $H^+$ | 5.85 | $k$ A | 25 | 2.38 | -4 |
| | | | | 5.95 | | " | 1.73 | -4 |
| | | 12.5 | " | 6.47 | " | " | 1.20 | -4 |
| | | | | 6.03 | | " | 3.23 | -4 |
| | | | | 5.10 | | " | 2.42 | -3 |
| .2 | $C_4H_9OC{:}CH + H_2O \rightarrow C_4H_9OCOCH_3$ | $H_2O + C_2H_5OH$ 42.7 wt % | $H^+$ | 6.27 | $k$ A | 25 | 1.49 | -4 |
| | | | | 5.96 | | " | 3.04 | -4 |
| .3 | $C_6H_5OC{:}CH + H_2O \rightarrow C_6H_5OCOCH_3$ | $H_2O + C_2H_5OH$ 42.7 wt % | $H^+$ | 2.47 | $k$ A | 25 | 7.28 | -5 |
| | | | | 2.25 | | " | 1.16 | -4 |

## LITERATURE

T. J. Jacobs, S. Searles, Jr., *ACS* 1944, **66**, 686.



942151 O—51——38

# BOND SATURATION

## Proton addition to C:N bond

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $\Delta H_a$ | $\Delta S_a$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3CH{:}NO_2^- + H_2O \rightarrow CH_3CH_2NO_2 + OH^-$ | $H_2O$ | ~ 0.05 | *k* AB | 0 | 2.76 | -7 | 24.3 | + 3.0 |
| .2 | $CH_3CH{:}NO_2^- + NH_4^+ \rightarrow CH_3CH_2NO_2 + NH_3$ | $H_2O$ | ~ 0.05 | *k* AB | 0 | 3.17 | -5 | 24.9 | + 14.5 |
| .3 | $CH_3CH{:}NO_2^- + CH_3NH_3^+ \rightarrow CH_3CH_2NO_2 + CH_3NH_2$ | $H_2O$ | ~ 0.05 | *k* AB | 0 | 1.70 | -5 | 25.5 | + 15.9 |
| .4 | $CH_3CH{:}NO_2^- + (CH_3)_2NH_2^+ \rightarrow CH_3CH_2NO_2 + (CH_3)_2NH$ | $H_2O$ | ~ 0.05 | *k* AB | 0 | 4.57 | -5 | 24.8 | + 14.9 |
| .5 | $CH_3CH{:}NO_2^- + (CH_3)_3NH^+ \rightarrow CH_3CH_2NO_2 + (CH_3)_3N$ | $H_2O$ | ~ 0.05 | *k* AB | 0 | 5.74 | -4 | 21.1 | + 6.8 |

## COMMENTS

From reverse reaction (see 402.450).

## LITERATURE

R. G. Pearson, *ACS* 1948, **70**, 204

# ADDITION

## Bond saturation

## Addition of hydrogen halide to multiple bond

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $(CH_3)_2C{:}CH_2 + HCl$ | $C_7H_{16}$ | > 0.1 | | $kAB^3$ | 0 | 4.6 | -4 | * | (1) |
| | | " | A = B = 0.5 | $H_2O$ | $kAB$ | 0 | 4.3 | -5 | * | " |
| .2 | $CH_3OOCC{:}CCOOCH_3 + HBr$ → *trans* (*a*), *cis* (*b*) | $CH_3COOH$ | | (*a* + *b*) = | $kAB^2$ | 20 | 3.5 | -3 | * | (2) |
| | | $C_6H_6$ | | | " | " | 3.1 | -2 | | " |
| | | $C_6H_{14}$ | | | " | 0 | 8.7 | +1 | | " |
| | | $CH_3COOH$ | | LiBr | $kAB[Br^-]$ | 20 | 1.5 | -2 | | " |

## COMMENTS

(.1) The fourth-order and the second-order reactions, the latter catalyzed by $H_2O$ as an impurity, are competitive. By cooling to -80°C and warming up to 0°C, the reaction at 0°C is greatly accelerated. (.2) In $CH_3COOH$, $C_6H_{14}$, $CH_3NO_2$, and in pure liquid, reactions *a* and *b* occur in approximately equal amounts; in $C_6H_6$, reaction *b* is about 90 % of the total. Concentration and temperature have no effect on the orientation, nor have peroxides and antioxidants. Bromides shift the reaction in favor of *a*.

## LITERATURE

(1) F.R.Mayo, J.J.Katz, *ACS* 1947, **69**, 1339.

(2) I.V.Smirnov-Zamkov, E.A.Shilov, *DAN* 1949, **67**, 671.

# ADDITION

## Bond saturation

*Liquid phase*

### Halogen addition to multiple bond

Amounts are in M/l.
Rates are in M/l per sec.

Rate measured $-dB/dt$

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_2H_4 + Br_2$ | $CCl_4$ | 0.057 | | | $kAB$ | 0 | 1.8 | -2 | | * | (4) |
| | | | | | | | 25 | 1.7 | -4 | | | |
| | | " | " | $H_2O$ | 0.0005 | | " | 5.8 | -4 | | | |
| | | " | A = 0.006 - 0.014; | B ~ 0.02 | | | 0 | See Comments | | | * | (23) |
| | | | | | | | 18 | | | | | |
| .2 | $CH_2{:}CHBr + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 1.18 | -4 | | * | (11) |
| | | $CH_3COOH$ | B = 0.015 | LiCl | 0.5 | $kAB[Cl^-]$ | 40 | 5.40 | -3 | | | (15) |
| | | | A = 0.13 - 0.31 | | 0.1 | | " | 4.57 | -3 | | | |
| | | | | | 0.2 - 0.4 | | " | 4.39 | -3 | | | |
| .3 | $CH_2{:}CHCH_3 + Br_2$ | $CCl_4$ | | | | $kAB$ | 25 | 3.3 | -3 | | | (4) |
| .4 | $CH_2{:}CHCOOH + Cl_2$ | $CH_3COOH$ | A = B = 0.0125 - 0.025 | | | $kAB$ | 25 | 2.8 | -4 | | | (22) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $CH_2{:}CHCOOH + Br_2$ | $H_2O$ | A = B = | | | $kAB$ | 25 | | | | * | ([18]) |
| | | | 0.0125 | | | | (0.3) | 3.18 | 0 | | | |
| | | | " | | | | (0.6) | 1.66 | 0 | | | |
| | | | 0.0062 | | | | (0.2) | 4.85 | 0 | | | |
| | | | " | | | | (0.6) | 3.32 | 0 | | | |
| | | | 0.0125 | $H_2SO_4$ | 0.05 | " | (0.3) | 5.7 | -1 | | | " |
| | | | " | | " | | (0.6) | 3.8 | -1 | | | |
| | | | 0.0062 | " | " | " | (0.3) | 5.3 | -1 | | | " |
| | | | " | | " | | (0.6) | 3.8 | -1 | | | |
| | | $CH_3COOH + H_2O$ 25 % | 0.0125 | - | | " | (0.3) | 3.1 | -3 | | | " |
| | | | | | | | (0.6) | 2.7 | -3 | | | |
| | | 50 % | " | | | " | (0.3) | 4.8 | -2 | | | " |
| | | | | | | | (0.6) | 2.2 | -2 | | | |
| | | $CH_3COOH$ | A = B = | HBr | $HBr/Br_2$ | $kAB$ | 25 | | | | * | ([18]) |
| | | | 0.0125 | | 0.05 | | (0.3) | 5.8 | -4 | | | |
| | | | | | 0.125 | | (0.3) | 2.3 | -3 | | | " |
| | | | | | | | (0.6) | 2.3 | -3 | | | |
| | | | | | 0.25 | | (0.3) | 4.2 | -3 | | | " |
| | | | | | | | (0.6) | 4.0 | -3 | | | |
| | | | | | 0.5 | | (0.3) | 5.1 | -3 | | | " |
| | | | | | | | (0.6) | 5.3 | -3 | | | |
| | | | | | 1.0 | | (0.3) | 8.0 | -3 | | | " |
| | | | | | | | (0.6) | 7.3 | -3 | | | |
| | | | | | 2.0 | | (0.3) | 9.5 | -3 | | | " |
| | | | | | | | (0.6) | 7.3 | -3 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5 | $CH_2{:}CHCOOH + Br_2$ *(continued)* | | | | 4.0 | | (0.3) | 6.3 | -3 | | | ([18]) |
| | | | | | | | (0.6) | 5.1 | -3 | | | |
| | | | | | 5.0 | | (0.3) | 5.7 | -3 | | | " |
| | | | | | | | (0.6) | 5.3 | -3 | | | |
| | | $CH_3COOH$ | A = B = 0.0125 | HBr | 0.0125 | $k\,AB$ | 24 | 7.3 | -3 | | | ([10]) |
| .6 | $CH_2{:}CHCOOH + ICl \rightarrow CH_2ClCHICOOH$ | $CH_3COOH$ | A = B = 0.0125 - 0.05 | | | $k\,AB^2$ | 25 | 3.1 | -1 | | | |
| .7 | $CH_2{:}CHCH_2OH + I_2$ | $H_2O$ | A = 0.1 | | | $k\,B = (k_1\,[I_3^-] + k_2[I_2])A$ | | | | | * | ([3]) |
| | | | B = 0.01 - 0.04 | $I^-$ | 0.05 | $k$ | 0 | 6.1 | -6 | | | |
| | | | | | | | 15 | 3.55 | -5 | | | |
| | | | | | | | 30 | 1.44 | -4 | | | |
| | | | A = 0.1; B = 0.02 | " | 0.01 | $k$ | 15 | 5.0 | -5 | | | " |
| | | | | | 0.025 | | " | 4.1 | -5 | | | |
| | | | | | 0.05 | | " | 3.5 | -5 | | | |
| | | | | | 0.1 | | " | 3.2 | -5 | | | |
| | | | " | " | 0.01 - 1.0 | $k_1$ | 15 | 3.00 | -4 | | | " |
| | | | | | | $k_2$ | " | 1.67 | -3 | | | |
| | | $CH_3COOH$ | B / A | | | $k\,AB + k'AB^3$ | 25.0 | | | | * | ([16]) |
| | | | 0.023 / 0.283 | | | $k'$ | (1) | 3.93 | -3 | | | |
| | | | 0.027 / 0.577 | | | | " | 6.80 | -3 | | | |
| | | | 0.026 / 1.13 | | | | " | 1.13 | -2 | | | |
| | | | 0.024 / 2.35 | | | | " | 1.72 | -2 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o = 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $CH_2{:}CHCH_2OCOCH_3 + Br_2$ | $CH_3COOH$ | A = B = | | | $kAB + k'AB^2$ | 25.0 | | | | * | ([16]) |
| | | | 0.020 | | | $k$ | (1) | 2.65 | -1 | | | |
| | | | | | | | (f) | 1.30 | -1 | | | |
| | | | | | | $k'$ | (1) | 2.23 | +1 | | | |
| | | | | | | | (f) | 5.00 | +1 | | | |
| | | | 0.004 | | | $k$ | (1) | 1.13 | -1 | | | |
| | | | | | | | (f) | 1.00 | -1 | | | |
| | | | | | | $k'$ | (1) | 3.60 | +1 | | | |
| | | | | | | | (f) | 1.50 | +2 | | | |
| | | | | | | | 50.0 | | | | | |
| | | | 0.020 | | | $k$ | (1) | 4.80 | -1 | | | |
| | | | | | | | (f) | 4.50 | -1 | | | |
| | | | | | | $k'$ | (1) | 4.60 | +1 | | | |
| | | | | | | | (f) | 1.82 | +2 | | | |
| | | | 0.008 | | | $k$ | (1) | 4.13 | -1 | | | |
| | | | | | | | (f) | 4.50 | -1 | | | |
| | | | | | | $k'$ | (1) | 7.40 | +1 | | | |
| | | | | | | | (f) | 3.50 | +2 | | | |
| | | | 0.004 | | | $k$ | (1) | 2.92 | -1 | | | " |
| | | | | | | | (f) | 4.05 | -1 | | | |
| | | | | | | $k'$ | (1) | 1.11 | +2 | | | |
| | | | | | | | (f) | 6.80 | +2 | | | |
| | | | | | | | 70.0 | | | | | |
| | | | 0.008 | | | $k$ | (1) | 6.90 | -1 | | | " |
| | | | | | | | (f) | 7.28 | -1 | | | |
| | | | | | | $k'$ | (1) | 1.24 | +2 | | | |
| | | | | | | | (f) | 4.63 | +2 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $CH_2{:}CHCH_2OCOCH_3 + Br_2$ *(continued)* | | 0.004 | | | $k$ | (1) | 6.56 | -1 | | | |
| | | | | | | | (f) | 1.00 | 0 | | | |
| | | | | | | $k'$ | (1) | 2.50 | +2 | | | |
| | | | | | | | (f) | 6.06 | +3 | | | |
| | | | B A | | | | 25.0 | | | | | (16) |
| | | | 0.020 0.020 | | | $k$ | (1) | 2.65 | -1 | | | |
| | | | " " | | | $k'$ | " | 2.15 | +1 | | | |
| | | | 0.013 0.011 | | | $k$ | " | 2.00 | -1 | | | |
| | | | " " | | | $k'$ | " | 2.25 | +1 | | | |
| | | | 0.090 0.012 | | | $k$ | " | 1.58 | -1 | | | |
| | | | " " | | | $k'$ | " | 3.05 | +1 | | | |
| | | | 0.004 0.004 | | | $k$ | " | 1.13 | -1 | | | |
| | | | " " | | | $k'$ | " | 3.60 | +1 | | | |
| | | $CH_3COOH$ | A = B = 0.0125 - 0.05 | | | $kAB^2$ | 25 | 8.1 | +1 | | * | (18) |
| | | | | | | | 50 | 1.15 | +2 | 2.7 | | |
| | | $CCl_4$ | | 0.0125 | | $kAB$ | 25 | | | | | " |
| | | | | | | | (0.2) | 2.3 | -4 | | | |
| | | | | | | | 0 | | | | | |
| | | | | 0.025 | | | (0.2) | 2.3 | -2 | | | |
| | | | | | | | (0.6) | 3.8 | -2 | | | |
| | | | | | | | 25 | | | | | |
| | | | | | | | (0.2) | 1.16 | -2 | | | |
| | | | | | | | (0.6) | 2.50 | -2 | | | |
| | | | | | | | 50 | | | | | |
| | | | | | | | (0.2) | 1.3 | -3 | | | |
| | | | | | | | (0.6) | 8.4 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o = 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .9 | $CH_2{:}CHCH_2OCOCH_3 + I_2$ | $CH_3COOH$ | B | A | | $kAB + k'AB^3$ | | 25.0 | | | | * | ([16]) |
| | | | 0.016 | 1.48 | | | $k'$ | (1) | 1.21 | -3 | | | |
| | | | " | " | | | | (0.5) | 1.46 | -3 | | | |
| | | | 0.018 | 0.416 | | | " | (1) | 1.39 | -3 | | | |
| | | | " | " | | | | (0.5) | 2.62 | -3 | | | |
| | | | 0.057 | 1.48 | | | " | (1) | 1.81 | -3 | | | |
| | | | " | " | | | | (0.5) | 3.53 | -3 | | | |
| | | | 0.060 | 0.371 | | | " | (1) | 2.39 | -3 | | | |
| | | | " | " | | | | (0.5) | 3.33 | -3 | | | |
| | | | 0.083 | 0.016 | | | " | (1) | 3.68 | -3 | | | |
| | | | " | " | | | | (0.5) | 2.70 | -3 | | | |
| | | $CH_3COOH$ | A ~ 0.4 | | | | $kAB$ | 25 | 2.57 | -5 | | | ([15]) |
| | | | B ~ 0.018 | | $CH_3COONa$ | 0.100 | " | " | 5.39 | -5 | | | |
| | | | | | LiCl | " | " | " | 9.35 | -5 | | | |
| | | | | | HI | " | " | " | 1.05 | -4 | | | |
| .10 | $CH_2{:}CHCH_2OCOCH_3 + ICl \rightarrow CH_3COOCH_2CHICH_2Cl$, $\rightarrow CH_3COOCH_2CHClCH_2I$ | $CH_3COOH$ | A = B = 0.0125 - 0.025 | | | | $kAB^2$ | 25 | 7.8 | -1 | | * | ([22]) |
| | | " | " | | HCl | HCl/ICl | $kAB$ | 25 | | | | | " |
| | | | | | | 0 | | (0.2) | 4.5 | 0 | | | |
| | | | | | | | | (0.6) | 2.5 | 0 | | | |
| | | | | | | 0.25 | | (0.2) | 2.8 | 0 | | | |
| | | | | | | | | (0.6) | 2.2 | 0 | | | |
| | | | | | | 1.0 | | (0.2) | 2.2 | 0 | | | |
| | | | | | | | | (0.6) | 1.6 | 0 | | | |
| | | | | | | 2.0 | (0.2) - | (0.6) | 1.4 | 0 | | | |
| | | | | | | 8.0 | " | | 2.4 | -1 | | | |
| | | | | | | 16 | " | | 2.1 | -1 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $CH_2{:}CHCH_2OCOC_6H_5 + Br_2$ | $C_6H_5Cl$ | A = B = 0.0125 - 0.1 | | | $kAB^2$ | 24 | 1.1 | 0 | | * | ([5]) |
| | | $CHCl_3$ | 0.1 | | | $kAB^2$ | 24 | 7.4 | -1 | | * | " |
| | | $CCl_4$ | A = B = | | | $kAB$ | 24 | | | | | |
| | | | 0.2 | | | | (0.1) | 8.3 | -3 | | * | " |
| | | | | | | | (0.4) | 3.5 | -3 | | | |
| | | | 0.1 | | | | (0.1) | 1.5 | -3 | | * | " |
| | | | | | | | (0.4) | 8.1 | -4 | | | |
| | | $CH_3COOH$ | A = B = 0.0125 - 0.05 | | | $kAB^2$ | 25 | 7.1 | +1 | | | ([18]) |
| | | | | | | | 50 | 1.2 | +2 | 3.9 | | |
| .12 | $CH_2{:}CHCH_2OCOCH_2Cl + Br_2$ | $CH_3COOH$ | A = B = 0.0125 - 0.05 | | | $kAB^2$ | 25 | 3.5 | +1 | | * | ([18]) |
| | | | | | | | 50 | 4.35 | +1 | | | |
| | | $CCl_4$ | A = B = | | | $kAB$ | 25 | | | | | " |
| | | | 0.05 | | | | (0.2) | 2.3 | -2 | | | |
| | | | 0.025 | | | | " | 4.6 | -3 | | | |
| | | | 0.0125 | | | | " | 1.3 | -4 | | | |
| | | | 0.0062 | | | | " | 5.0 | -5 | | | |
| | | " | A = B = | | | " | 0 | | | | | " |
| | | | 0.025 | | | | (0.2) | 5.8 | -3 | | | |
| | | | | | | | (0.6) | 8.3 | -3 | | | |
| | | | | | | | 25 | | | | | |
| | | | " | | | | (0.2) | 4.6 | -3 | | | |
| | | | | | | | (0.6) | 7.0 | -3 | | | |
| | | | | | | | 50 | | | | | |
| | | | " | | | | (0.2) | 4.1 | -4 | | | |
| | | | | | | | (0.6) | 2.7 | -4 | 1.6 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .12 | $CH_2{:}CHCH_2OCOCH_2Cl + Br_2$ *(continued)* | $CCl_4$ | A = B = 0.025 | HBr | $HBr/Br_2$ | $k$AB | 25 | | | | * | ([18]) |
| | | | | | 0.167 | | (0.2) | 1.16 | -1 | | | |
| | | | | | " | | (0.6) | 5.0 | -2 | | | |
| | | | | | 0.33 | | (0.2) | 3.0 | -1 | | | |
| | | | | | " | | (0.6) | 1.16 | -1 | | | |
| | | | | | 0.66 | | (0.2) | 3.3 | -1 | | | |
| | | | | | " | | (0.6) | 1.0 | -1 | | | |
| | | | 0.0125 | " | 0.33 | " | (0.2) | 6.7 | -2 | | | " |
| | | | | | " | | (0.6) | 3.3 | -2 | | | |
| | | | | | 0.66 | | (0.2) | 1.16 | -1 | | | |
| | | | | | " | | (0.6) | 5.0 | -2 | | | |
| | | | | | 2.0 | | (0.2) | 5.5 | -1 | | | |
| | | | | | " | | (0.5) | 1.5 | -1 | | | |
| | | | | | 4.0 | | (0.2) | 2.8 | -1 | | | |
| | | | | | " | | (0.5) | 1.16 | -1 | | | |
| | | | 0.0062 | " | 2.0 | " | (0.2) | 1.33 | -1 | | | " |
| | | | | | " | | (0.6) | 6.6 | -2 | | | |
| | | | | | 4.0 | | (0.2) | 2.16 | -1 | | | |
| | | | | | " | | (0.6) | 1.33 | -1 | | | |
| .13 | $CH_2{:}CHCH_2Cl + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 5.61 | -4 | | * | ([11]) |
| | | $CH_3COOH$ | A = B = 0.008 | | | $k$AB | 25 | 2.00 | -1 | | | ([15]) |
| | | | " | $CH_3COONa$ | 0.100 | " | " | 2.75 | -1 | | | |
| | | | " | $H_2SO_4$ | " | " | " | 3.20 | -1 | | | |
| | | | " | $NaNO_3$ | " | " | " | 5.80 | -1 | | | |
| | | | " | LiCl | " | " | " | 1.44 | 0 | | | |
| | | | " | LiBr | " | " | " | 6.95 | -1 | | | |
| | | | " | HBr | " | " | " | 6.95 | -1 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .13 | $CH_2{:}CHCH_2Cl + Br_2$ *(continued)* | $CH_3COOH$ | A = B = | | | $kAB + k'AB^2$ | 25.0 | | | | * | ([16]) |
| | | | 0.020 | | | $k$ | (1) | 5.5 | -2 | | | |
| | | | | | | | (f) | 3.0 | -2 | | | |
| | | | | | | $k'$ | (1) | 2.90 | 0 | | | |
| | | | | | | | (f) | 1.00 | +1 | | | |
| | | | 0.008 | | | $k$ | (1) | 2.0 | -2 | | | " |
| | | | | | | | (f) | 2.0 | -2 | | | |
| | | | | | | $k'$ | (1) | 2.25 | 0 | | | |
| | | | | | | | (f) | 1.10 | +1 | | | |
| | | | | | | | 50.0 | | | | | |
| | | | 0.020 | | | $k$ | (1) | 9.0 | -2 | | | " |
| | | | | | | | (f) | 8.5 | -2 | | | |
| | | | | | | $k'$ | (1) | 5.40 | 0 | | | |
| | | | | | | | (f) | 2.50 | +1 | | | |
| | | | 0.008 | | | $k$ | (1) | 4.3 | -2 | | | " |
| | | | | | | | (f) | 5.6 | -2 | | | |
| | | | | | | $k'$ | (1) | 7.30 | 0 | | | |
| | | | | | | | (f) | 5.00 | +1 | | | |
| | | | | | | | 70.0 | | | | | |
| | | | 0.020 | | | $k$ | (1) | 1.38 | -1 | | | " |
| | | | | | | | (f) | 1.63 | -1 | | | |
| | | | | | | $k'$ | (1) | 8.75 | 0 | | | |
| | | | | | | | (f) | 6.50 | +1 | | | |
| | | | 0.004 | | | $k$ | (1) | 5.6 | -2 | | | " |
| | | | | | | | (f) | 3.26 | -1 | | | |
| | | | | | | $k'$ | (1) | 1.85 | +1 | | | |
| | | | | | | | (f) | 1.75 | +2 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .13 | $CH_2{:}CHCH_2Cl + Br_2$ *(continued)* | | B A | | | | 25.0 | | | | | |
| | | | 0.040 0.040 | | | $k'$ | (1) | 4.58 | 0 | | | ([16]) |
| | | | 0.040 0.020 | | | | " | 4.50 | 0 | | | |
| | | | 0.020 0.040 | | | | " | 2.95 | 0 | | | |
| | | | 0.020 0.020 | | | | " | 2.90 | 0 | | | |
| | | | 0.008 0.008 | | | | " | 2.25 | 0 | | | |
| | | $CH_3COOH + H_2O$ 0.2 % | A = B = 0.008 | | | $k$ | 25.0 | 2.0 | -2 | | | " |
| | | 1.0 | | | | | (1) | 3.2 | -2 | | | |
| | | 5.0 | | | | | " | 1.8 | -1 | | | |
| .14 | $CH_2{:}CHCH_2Br + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 2.04 | -3 | | * | ([11]) |
| .15 | $CH_3CH{:}CHBr + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 7.68 | -5 | | * | ([11]) |
| .16 | $CH_3CH_2CH{:}CH_2 + Br_2$ | $CCl_4$ | | | | $k$AB | 25 | 3.3 | -2 | | | ([4]) |
| .17 | $CH_3CH{:}CHCH_3 + Br_2$ | $CCl_4$ | | | | $k$AB | 25 | 1.0 | 0 | | | ([4]) |
| .18 | $(CH_3)_2C{:}CH_2 + Br_2$ | $CCl_4$ | | | | $k$AB | 25 | 1.0 | 0 | | | ([4]) |
| .19 | $CH_3CH{:}CHCHO + Cl_2$ | $CH_3COOH$ | A = B = 0.0125 | - | | $k$AB | 25 | 7.0 | -1 | | | ([22]) |
| | | | | HCl | 0.0062 | | " | 5.8 | 0 | | | |
| | | | | $H_2SO_4$ | 0.0125 | | " | 1.0 | -2 | | | |
| .20 | *trans* - $CH_3CH{:}CHCOOH + Br_2$ (crotonic acid) | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $k$AB | | | | | * | ([13]) |
| | | | | | 0 | | 24 | <1.0 | -4 | | | |
| | | | | | 0.25 | | " | 3.0 | -4 | | | |
| | | | | | 0.50 | | " | 5.0 | -4 | | | |
| | | | | | 1.0 - 4.0 | | " | 8.5 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .20 | *trans* - $CH_3CH{:}CHCOOH + Br_2$ *(continued)* (crotonic acid) | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 3 - 7 | -9 | | * | ([19]) |
| | | | | | | | " | 1.3 - 1.7 | -9 | | * | ([20]) |
| | | " | A = B = 0.033 | | | $k$AB | 13 | | | | * | ([24]) |
| | | | | | | | (1) | 1.75 | -5 | | | |
| | | | | | | | (f) | 3.3 | -5 | | | |
| | | " | " | HBr | $HBr/Br_2$ 0.53 | " | (1) | 1.65 | -3 | | | " |
| | | | | | | | (f) | 2.7 | -4 | | | |
| | | " | " | $H_2O$ | 70 % sat | " | (1) | 4.8 | -4 | | | " |
| | | | | | | | (f) | 6.8 | -4 | | | |
| | | $CH_3COOH$ | A = B ~ 0.07 | | | $k$AB; | $k'AB^2$ 35.5 | | | | * | ([1]) |
| | | | | | | $k$ | (0.1) | 2.7 | -4 | | | |
| | | | | | | | (0.5) | 5.3 | -4 | | | |
| | | | | | | $k'$ | (0.1) | 1.7 | -2 | | | |
| | | | | | | | (0.5) | 6.3 | -2 | | | |
| | | | " | HBr | $HBr/Br_2$ 1.05 | $k$ | (0.1) | 2.8 | -4 | | | " |
| | | | | | | | (0.5) | 5.6 | -4 | | | |
| | | | | | " | $k'$ | (0.1) | 1.8 | -2 | | | |
| | | | | | | | (0.5) | 6.9 | -2 | | | |
| | | | " | " | 2.10 | $k$ | (0.1) | 3.2 | -4 | | | " |
| | | | | | | | (0.5) | 5.8 | -4 | | | |
| | | | | | " | $k'$ | (0.1) | 2.0 | -2 | | | |
| | | | | | | | (0.5) | 7.0 | -2 | | | |



942151 O—51——39

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .20 | *trans* - $CH_3CH{:}CHCOOH + Br_2$ *(continued)* (crotonic acid) | | A = B = ~ 0.07 | HBr | 6.90 | $k$ | (0.1) | 9.0 | -4 | | | ([1]) |
| | | | | | | | (0.5) | 9.6 | -4 | | | |
| | | | | | | $k'$ | (0.1) | 5.7 | -2 | | | |
| | | | | | | | (0.5) | 1.15 | -1 | | | |
| | | | | ICl | $ICl/Br_2$ 0.95 | $k$ | (0.1) | 1.8 | -4 | | | " |
| | | | | | | | (0.5) | 6.3 | -4 | | | |
| | | | | | " | $k'$ | (0.1) | 2.1 | -2 | | | |
| | | | | | | | (0.5) | 7.6 | -2 | | | |
| | | | | " | 7.80 | $k$ | (0.1) | 8.7 | -4 | | | " |
| | | | | | | | (0.5) | 9.4 | -4 | | | |
| | | | | | | $k'$ | (0.1) | 5.5 | -2 | | | |
| | | | | | | | (0.5) | 1.1 | -1 | | | |
| | | | | $SbBr_3$ | $SbBr_3/Br_2$ 1.0 | $k$ | (0.1) | 2.3 | -4 | | | " |
| | | | | | | | (0.5) | 5.0 | -4 | | | |
| | | | | | | $k'$ | (0.1) | 1.4 | -2 | | | |
| | | | | | | | (0.5) | 6.0 | -2 | | | |
| | | | | " | 6.40 | $k$ | (0.1) | 1.7 | -4 | | | " |
| | | | | | | | (0.5) | 3.2 | -4 | | | |
| | | | | | | $k'$ | (0.1) | 1.1 | -2 | | | |
| | | | | | | | (0.5) | 2.6 | -2 | | | |
| .21 | *trans* - $CH_3CH{:}CHCONH(p - C_6H_4Br) + Br_2$ | $CH_3COOH$ | A = B = 0.025 | | | $k$ AB | 25 | | | | | ([18]) |
| | | | | | | | (0.2) | 3.0 | -3 | | | |
| | | | | | | | (0.4) | 4.5 | -3 | | | |
| | | | | | | | (0.6) | 6.3 | -3 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .21 | *trans* - $CH_3CH{:}CHCONH(p - C_6H_4Br) + Br_2$ *(continued)* | | 0.0125 | | | | (0.2) | 1.7 | -3 | | | |
| | | | | | | | (0.4) | 2.8 | -3 | | | |
| | | | | | | | (0.6) | 4.3 | -3 | | | |
| .22 | *cis* - $COOHCH{:}CHCOOH + Cl_2$ | $H_2O$ | A = 0.1 - 0.6; B = 0.002 - 0.02 | HCl | 0.1 - 1.0 | $kAB/[H^+]$ | 25 | 8.7 - 10 | -4 | | * | ([21]) |
| | | $H_2O$ | A = 0.19; $10^2B$ = | HCl 1.0 + $Fe^{++}$; $Fe^{++}$ added at rate $R$ | | $k'A^{1/2}B^{1/2}$ | | | | | | |
| | | | 0.138 | $10^6R$ = 5.7 | | | 25 | 4.6 | -1 | | * | " |
| | | | 0.591 | " | | | " | 3.1 | -1 | | | |
| | | | 0.096 | | 0.55 | | " | 1.6 | -1 | | | |
| | | " | 3.46 | | 5.6 | $k''AR^{1/2}$ | 25 | 1.45 | 0 | | | |
| | | | 1.41 | | " | | " | 1.25 | 0 | | | |
| .23 | *cis* - $COOHCH{:}CHCOOH + Br \rightarrow$ *rac* | $H_2O$ | A = 0.1 | KBr | 1.0 | $kB = (k_1A + k_2A^-)B$ | | | | | * | ([3]) |
| | | B = 0.02 | | | | $k$ | 25 | 9.3 | -5 | | | |
| | (A = $COOHCH{:}CHCOOH$ | | | | | $k_1$ | " | 1.76 | -5 | | | |
| | $A^-$ = $COOHCH{:}CHCOO^-$) | | | | | $k_2$ | " | 2.4 | -3 | | | |
| | | B = 0.02; | A = 0.05 | HCl 1.0 + KBr 1.0 | | $k$ | 25 | 2.2 | -6 | | | " |
| | | | 0.1 | | | | " | 4.25 | -6 | | | |
| | | | 0.2 | | | | " | 8.6 | -6 | | | |
| | | B = 0.02; | A = 0.1 | HCl 0.125 + KBr 1.0 | | $k$ | 25 | 2.34 | -5 | | | " |
| | | | | 0.25 " | | | " | 1.25 | -5 | | | |
| | | | | 0.5 " | | | " | 7.0 | -6 | | | |
| | | | | 1.0 " | | | " | 4.25 | -6 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .23 | *cis* - COOHCH:CHCOOH + $Br_2$ → *rac (continued)* | B = 0.02; | A = 0.05 | HCl 1.0 + | KBr 0.125 | $k$ | 25 | 5.0 | -6 | | | ([3]) |
| | | | | " | 0.25 | | " | 3.7 | -6 | | | |
| | | | | " | 0.5 | | " | 2.8 | -6 | | | |
| | | | | " | 1.0 | | " | 2.2 | -6 | | | |
| | | $CH_3COOH$ | A = 0.13; B = 0.01 | KBr | 0.2 | $kA[Br_3^-] = k'AB[Br^-]$ | | | | | * | ([14]) |
| | | | | | | $k$ | 30 | 5.90 | -4 | | | |
| | | | | | | | 50 | 3.04 | -3 | | | |
| | | | | | | | 70 | 1.45 | -2 | 9.0 | | |
| | | | | | | $k'$ | 30 | 3.28 | -2 | | | |
| | | | | | | | 50 | 8.29 | -2 | | | |
| | | | | | | | 70 | 2.01 | -1 | 9.3 | | |
| | | $CH_3COOH$ | A = 0.0126 | HBr | $HBr/Br_2$ | $kAB$ | | | | | * | ([13]) |
| | | | | | 1 | | 24 | 4.5 | -3 | | | |
| | | | | | 4 | | | 9.3 | -3 | | | |
| .24 | *trans* - COOHCH:CHCOOH + $Br_2$ → *meso* | $H_2O$ | A = 0.0215 | | | $kB = (k_1A + k_2A^-)B$ | | | | | * | ([3]) |
| | ($A^-$ = COOHCH:$CHCOO^-$ A = COOHCH:CHCOOH) | | B = 0.003 - 0.012 | HCl 0.2 + | KBr 1.0 | $k$ | 25 | 3.9 | -6 | | | |
| | | | | | | $k_1$ | " | 1.55 | -4 | | | |
| | | | | | | $k_2$ | " | 5.0 | -3 | | | |
| | | | B = 0.004; A = 0.0086 | HCl 0.05 + | KBr 1.0 | $k$ | 25 | 2.0 | -6 | | | " |
| | | | 0.0172 | | | | " | 4.15 | -6 | | | |
| | | | B = 0.006; A = 0.0215 | HCl 0.4 | + KBr 1.0 | $k$ | 25 | 3.55 | -6 | | | " |
| | | | | 0.2 | " | | " | 3.84 | -6 | | | |
| | | | | 0.1 | " | | " | 4.30 | -6 | | | |
| | | | | 0.05 | " | | " | 5.15 | -6 | | | |
| | | | | 0.025 | " | | " | 7.50 | -6 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .24 | *trans* - COOHCH:CHCOOH + $Br_2$ → *meso* *(continued)* | B = 0.01; | A = 0.0173 | HCl 1.0 + KBr | 0.005 | $k$ | 25 | 5.0 | -6 | | | ([3]) |
| | | | | " | 0.02 | | " | 2.82 | -6 | | | |
| | | | | " | 0.08 | | " | 2.42 | -6 | | | |
| | | | | " | 0.16 | | " | 2.52 | -6 | | | |
| | | | | " | 0.32 | | " | 2.86 | -6 | | | |
| | | | | " | 0.64 | | " | 2.95 | -6 | | | |
| | | $CH_3COOH$ | A = 0.13; | $kA\,[Br_3^-] = k'AB[Br^-]$ | | | | | | | * | ([14]) |
| | | | B = 0.01 | LiBr | 0.2 | $k$ | 30 | 1.15 | -4 | | | |
| | | | | | | | 50 | 6.09 | -4 | | | |
| | | | | | | | 70 | 3.06 | -3 | 9.4 | | |
| | | | | | | $k'$ | 30 | 6.35 | -3 | | | " |
| | | | | | | | 50 | 1.66 | -2 | | | |
| | | | | | | | 70 | 4.24 | -2 | 9.8 | | |
| | | | | HBr | 0.19 | $k$ | 30 | 8.73 | -4 | | | " |
| | | | | | | | 50 | 5.95 | -3 | | | |
| | | | | | | | 70 | 3.46 | -2 | 11.8 | | |
| | | | | | | $k'$ | 30 | 4.8 | -2 | | | " |
| | | | | | | | 50 | 1.62 | -1 | | | |
| | | | | | | | 70 | 4.80 | -1 | 11.4 | | |
| | | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $kAB$ | | | | | * | ([13]) |
| | | | | | 1 | | 24 | 3.2 | -4 | | | |
| | | | | | 4 | | " | 7.8 | -4 | | | |
| .25 | *trans* - COOHCH:$CHCOO^-$ + $Br_2$ | $H_2O$ | A = 0.0173; B = 0.008 | KBr | 1.0 | $kB$ | 25 | 8.5 | -4 | | | ([3]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .26 | $CH_2{:}CHCH_2CH_2Cl + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 8.87 | -3 | | * | (11) |
| .27 | $CH_2{:}CHCH_2CH_2Br + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 4.02 | -2 | | * | (11) |
| .28 | $CH_3CH{:}CHCH_2Br + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 1.46 | -3 | | * | (11) |
| .29 | $(CH_3)_2C{:}CHCH_3 + Br_2$ | $CCl_4$ | | | | $k$AB | 25 | 4.1 | 0 | | | (4) |
| .30 | $CH_2{:}CHCH_2CH_2COOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 4 - 6 | -2 | | | (19) |
| .31 | $CH_3CH{:}CHCH_2COOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 3 - 16 | -3 | | | (19) |
| .32 | $C_2H_5CH{:}CHCOOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 0.9 - 1.7 | -8 | | | (19) |
| .33 | *cis* - $CH_3CH{:}C(CH_3)COOH + Br_2$ (angelic acid) | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 2 - 5 | -8 | | | (19) |
| | | $CH_3COOH$ | See Supplementary Table | | | | | | | | | |
| .34 | $CH_3CH{:}C(CH_3)COOH + Br_2$ (tiglic acid) | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 0.4 - 2.8 | -8 | | | (19) |
| .35 | $(CH_3)_2C{:}CHCOOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 0.9 - 2 | -6 | | | (19) |
| | | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $k$AB | | | | | * | (13) |
| | | | | | 0 - 0.5 | | 24 | 2.5 | -3 | | | |
| | | | | | 1.0 - 4.0 | | " | 3.0 | -3 | | | |
| .36 | $COOHCH_2CH{:}CHCOOH + Br_2$ | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $k$AB | | | | | * | (13) |
| | | | | | 1 | | 24 | 1.5 | -3 | | | |
| | | | | | 4 | | " | 7.3 | -3 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .37 | $COOHC(CH_3):CHCOOH + Br_2$ (citraconic acid) | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $kAB$ | | | | | * | (13) |
| | | | | | 1 | | 24 | 9.0 | -5 | | | |
| | | | | | 4 | | " | 2.0 | -4 | | | |
| .38 | $COOHC(CH_3):CHCOOH + Br_2$ (mesaconic acid) | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $kAB$ | | | | | * | (13) |
| | | | | | 1 | | 24 | 2.3 | -4 | | | |
| | | | | | 4 | | " | 4.1 | -4 | | | |
| .39 | $CH_2:CHCH_2CH_2CH_2Br + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 6.7 | -1 | | * | (11) |
| .40 | $CH_3CH:CHCH:CHCOOH + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 0.3 - 3 | -5 | | | (19) |
| .41 | *allo* - $CH_3CH:CHCH:CHCOOH + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 0.8 - 1 | -5 | | | (19) |
| .42 | $C_2H_5CH:CHCH_2COOH + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 0.3 - 1 | -1 | | | (19) |
| .43 | $(CH_3)_2C:C(CH_3)COOH + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 3 - 8 | -8 | | | (19) |
| .44 | $COOHCH_2C(CH_3):CHCOOH + Br_2$ | $CH_3COOH$ | A = 0.0125 | HBr | $HBr/Br_2$ | $kAB$ | | | | | * | (13) |
| | | | | | 1 | | 24 | 2.5 | -4 | | | |
| | | | | | 4 | | " | 8.1 | -4 | | | |
| .45 | $CH_2:CH(CH_2)_8COOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $kAB$ | 15 | 1.5 - 4 | -4 | | | (19) |
| .46 | $CH_3CH:CH(CH_2)_7COOH + Br_2$ | $CCl_4$ | A = B = 0.0031 | | | $kAB$ | 25 | 2.7 | -2 | | * | (18) |
| | | | | | | | 50 | 1.2 | -2 | | | |
| | | $CH_3COOH$ | " | | | $kAB^2$ | | | | 3.0 | | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .47 | *cis* - $C_8H_{17}CH{:}CH(CH_2)_7COOH + Br_2$ (oleic acid) | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 4 - 8 | -3 | | * | (19) |
| | | " | A = B = 0.033 | | | $k$AB | 13 | | | | | |
| | | | | | | | (1) | 2.2 | +1 | | * | (24) |
| | | | | | | | (f) | 2.2 | -1 | | | |
| .48 | *trans* - $C_8H_{17}CH{:}CH(CH_2)_7COOH + Br_2$ (elaidic acid) | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 0.8 - 3 | -3 | | * | (19) |
| | | " | A = B = 0.033 | | | $k$AB | 13 | | | | * | (24) |
| | | | | | | | (1) | 2.8 | +1 | | | |
| | | | | | | | (f) | 1.1 | 0 | | | |
| .49 | $C_8H_{17}CH{:}CH(CH_2)_{11}COOH + Br_2$ (erucic acid) | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 0.8 - 3 | -3 | | | (19) |
| .50 | $C_8H_{17}CH{:}CH(CH_2)_{11}COOH + Br_2$ (brassidic acid | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 0.8 - 2 | -3 | | | (19) |
| .51 | $C_{15}H_{31}CH{:}CHCOOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $k$AB | 15 | 6.8 | -9 | | | (19) |
| | **Aryl-substituted olefins** | | | | | | | | | | | |
| .52 | $C_6H_5CH{:}CHC_6H_5 + Br_2$ | $CH_3OH$ | A = 0.01 | $k$AB; | $k_1A[Br_3^-] + k_2AB$ | | 0 | | | | * | (2) |
| | | | | KBr | 0 | | $k_2$ | 3.3 | 0 | | | |
| | | | | " | 0.0186 | | $k$ | 3.95 | -1 | | | |
| | | | | | 0.114 | | " | 1.02 | -1 | | | |
| | | | | | 0.205 | | " | 7.0 | -2 | | | |
| | | | | | 0.500 | | " | 5.0 | -2 | | | |
| | | | | " | 0.02 - 0.5 | | $k_1$ | 3.3 | -2 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .53 | $C_6H_5CH{:}CHCHO + Cl_2$ | $CH_3COOH$ | A = B = 0.025 | – | | $k$AB | 25 | 8.3 | -2 | | | (22) |
| | | | | HCl | 0.1 | | " | 3.5 | -1 | | | |
| | | | | $H_2SO_4$ | 0.1 | | " | 3.3 | -1 | | | |
| .54 | *cis* – $C_6H_5CH{:}CHCOOH + Cl_2$ | $CH_3COOH$ | A = B = 0.05 – 0.00625 | | | $k$AB | 25 | 3.5 | -1 | | | (22) |
| | | $C_6H_5NO_2$ | 0.00625 | | | " | " | 1.25 | 0 | | | " |
| | | $CH_3COOH$ 20 % + $CCl_4$ 80 % | 0.025 | | | " | " | 2.0 | -3 | | | " |
| .55 | *trans* – $C_6H_5CH{:}CHCOOH + Cl_2$ | $CH_3COOH$ | A = B = 0.025 | | | $k$AB | 15 | 5.7 | -2 | | | (22) |
| | | | 0.0125 | | | | " | 4.5 | -2 | | | |
| | | | 0.05 | | | | 25 | 1.0 | -1 | | | |
| | | | 0.025 | | | | " | 9.5 | -2 | | | |
| | | | 0.0125 | | | | " | 8.2 | -2 | | | |
| | | | 0.00625 | | | | " | 7.2 | -2 | | | |
| | | $C_6H_5NO_2$ | 0.025 | | | " | 15 | 5.8 | -2 | | | " |
| | | | 0.00625 | | | | " | 5.0 | -2 | | | |
| | | | 0.025 | | | | 25 | 9.0 | -2 | | | |
| | | | 0.0125 | | | | " | 8.2 | -2 | | | |
| | | | 0.00625 | | | | " | 7.7 | -2 | | | |
| .56 | *cis* – $C_6H_5CH{:}CHCOOH + Br_2$ | $CH_3COOH$ | A = B = | | | $k$AB$^2$ | 25 | 3.5 | -1 | | | (18) |
| | | | 0.0125 – 0.05 | | | | 50 | 7.8 | -1 | 5.8 | | |
| | | " | A = B = 0.0125 | HBr | $HBr/Br_2$ | $k$AB | 25 | | | | | " |
| | | | | | 0 | | (0.2) | 1.08 | -3 | | | |
| | | | | | " | | (0.5) | 6.3 | -4 | | | |
| | | | | | 0.125 | | (0.2) | 1.08 | -3 | | | |
| | | | | | " | | (0.5) | 7.5 | -4 | | | |
| | | | | | 0.25 | | (0.2) | 1.1 | -3 | | | |
| | | | | | " | | (0.5 | 8.2 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .56 | *cis* - $C_6H_5CH{:}CHCOOH + Br_2$ *(continued)* | | | | 0.5 | | (0.2) | 1.1 | -3 | | | |
| | | | | | " | | (0.5) | 8.3 | -4 | | | |
| | | $CH_3COOH + H_2O$ 10 % | A = B = | | | $kAB$ | 25 | | | | * | ([11]) |
| | | | 0.0125 | $H_2SO_4$ | 0.05 | | (0.2) | 1.85 | -1 | | | |
| | | | | | | | (0.4) | 1.4 | -1 | | | |
| | | | | | | | (0.6) | 9.0 | -2 | | | |
| | | " | 0.0062 | " | " | " | (0.2) | 1.15 | -1 | | | " |
| | | | | | | | (0.4) | 9.0 | -2 | | | |
| | | | | | | | (0.6) | 8.3 | -2 | | | |
| | | 25 % | 0.0125 | - | | " | (0.3) | 2.5 | 0 | | | " |
| | | | | | | | (0.4) | 1.9 | 0 | | | |
| | | | | | | | (0.5) | 1.7 | 0 | | | |
| | | " | " | $H_2SO_4$ | 0.05 | " | (0.2) | 1.1 | 0 | | | " |
| | | | | | | | (0.4) | 1.05 | 0 | | | |
| | | | | | | | (0.6) | 8.3 | -1 | | | |
| .57 | *trans* - $C_6H_5CH{:}CHCOOH + Br_2$ | $CH_3COOH$ | A = B = | | | $kAB$ | 25 | | | | * | ([18]) |
| | | | 0.025 | | | | (0.2) | 5.8 | -4 | | | |
| | | | " | | | | (0.4) | 5.8 | -4 | | | |
| | | | 0.0125 | | | " | (0.2) | 2.8 | -4 | | | |
| | | | " | | | | (0.4) | 2.7 | -4 | | | |
| | | | | HBr | $HBr/Br_2$ | | | | | | | |
| | | | " | | 0.125 | " | (0.2) | 1.10 | -3 | | | |
| | | | | | | | (0.5) | 7.7 | -4 | | | |
| | | | " | | 0.25 | " | (0.2) | 1.1 | -3 | | | |
| | | | | | | | (0.5) | 7.5 | -4 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .57 | *trans* - $C_6H_5CH{:}CHCOOH + Br_2$ *(continued)* | $CCl_4$ | | | | $k$AB | 0 | 4.8 - 1.1 | -5 | | | (8) |
| | | $CCl_4$ | | | | $k$AB | 15 | 3 - 7 | -8 | | * | (19) |
| | | $CCl_4$ | A = B = 0.033 | | | $k$AB | 0 | | | | * | (24) |
| | | | | | | | (1) | 1.1 | -5 | | | |
| | | | | | | | (f) | 2.7 | -5 | | | |
| | | | | | | | 13 | | | | | |
| | | | | | | | (1) | 1.8 | -5 | | | " |
| | | | | | | | (f) | 6.8 | -5 | | | |
| | | | | | | | 25.5 | | | | | |
| | | | | | | | (1) | 1.2 | -4 | | | " |
| | | | | | | | (f) | 1.9 | -4 | | | |
| | | $CHCl_3$ | " | | | " | 13 | | | | | |
| | | | | | | | (1) | 2.2 | -5 | | | " |
| | | | | | | | (f) | 2.2 | -4 | | | |
| | | " | A = B = 0.033 | HBr | $HBr/Br_2$ | $k$AB | 13 | | | | | (24) |
| | | | | | 0.26 | | (1) | 5 | -3 | | | |
| | | | | | " | | (f) | 4.3 | -3 | | | |
| | | | | | 0.53 | | (1) | 1.6 | -2 | | | " |
| | | | | | | | (f) | 2.0 | -2 | | | |
| | | | | | 1.08 | | (1) | 3.6 | -2 | | | " |
| | | | | | | | (f) | 4.3 | -2 | | | |
| | | | | HCl | $HCl/Br_2$ | | | | | | | |
| | | | | | 1.10 | | (1) | 1.3 | -4 | | | " |
| | | | | | | | (f) | 1.4 | -4 | | | |
| | | | | $H_2O$ | 70 % sat | | (1) | 4.6 | -5 | | | " |
| | | | | | | | (f) | 5.2 | -5 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o = 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .58 | *cis* - $C_6H_5CH{:}CHCOOH + BrCl \rightarrow$ ? | $CH_3COOH$ 20 % + $CCl_4$ 80 % | | | | $kAB$ | | | | | * | ([22]) |
| | | | A = 0.025; $Br_2/Cl_2$ = | | | | | | | | | |
| | | | 20 % reaction | | 0.25 | | 25 | 3.7 | -3 | | | |
| | | | 50 " | | " | | " | 3.2 | -3 | | | |
| | | | 20 % " | | 1.0 | | " | 7.0 | -3 | | | |
| | | | 50 " | | " | | " | 5.5 | -3 | | | |
| | | | 20 % " | | 2.0 | | " | 4.7 | -3 | | | |
| | | | 50 " | | " | | " | 3.5 | -3 | | | |
| .59 | *trans* - $C_6H_5CH{:}CHCOOH + BrCl$ | $CCl_4$ | $Br_2 = Cl_2$ | | | | 0 | 2.9 | -2 | | * | ([8]) |
| .60 | $C_6H_5CH{:}CHCOOCH_3 + Cl_2$ | $CH_3COOH$ | | | | $kAB$ | 24 | 1.7 | -1 | | | ([10]) |
| .61 | $C_6H_5CH{:}CHCOOCH_3 + Br_2$ | $CHCl_3$ | A = B = 0.033 | HBr | 0.015 | $kAB$ | 24 | 4.5 | -3 | | | ([10]) |
| | | $CCl_4$ | A = B = 0.016 | | | $kAB$ | 15 | 3 - 6.5 | -8 | | | ([19]) |
| | | " | A = B = 0.033 | | | $kAB$ | 13 | | | | * | ([24]) |
| | | | | | | | (1) | 1.1 | -5 | | | |
| | | | | | | | (f) | 1.75 | -5 | | | |
| .62 | $C_6H_5CH{:}CHCOOC_2H_5 + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $kAB$ | 15 | 3 - 7 | -8 | | | ([19]) |
| .63 | $C_6H_5CH{:}CHCH_2COOH + Br_2$ | $CCl_4$ | A = B = 0.016 | | | $kAB$ | 15 | 7 - 17 | -4 | | | ([19]) |
| .64 | $C_6H_5CH{:}C(CH_3)COOH + Br_2$ | $CCl_4$ | $Br_2 = Cl_2$ | | | $kAB$ | 0 | 3.3 | -6 | | | ([8]) |
| .65 | $C_6H_5CH{:}C(CH_3)COOH + BrCl$ | $CCl_4$ | $Br_2 = Cl_2$ | | | $kAB$ | 0 | 7 | -4 | | | ([8]) |
| .66 | $C_6H_5CH{:}CHCH_2CH_2COOH + Br_2$ | $CCl_4$ | | | | $kAB$ | 15 | 1 - 2.3 | -2 | | | ([19]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .67 | $C_6H_5CH{:}CHCH{:}CHCOOH + Br_2$ | $CCl_4$ | | | | $k$AB | 15 | 3 - 9 | -6 | | * | (19) |
| | | $CHCl_3$ | A = B = 0.033 | | | $k$AB | 13 | | | | * | (24) |
| | | | | | | | (i) | 2.5 | -1 | | | |
| | | | | | | | (f) | 4.9 | -2 | | | |
| .68 | $C_6H_5CH{:}CHCH{:}CHCOOH + Br_2$ | $CHCl_3$ | A = B = 0.033 | | | $k$AB | 13 | | | | | (24) |
| | | | | | | | (i) | 7.1 | -1 | | | |
| | | | | | | | (f) | 1.2 | -1 | | | |
| | | $CCl_4$ | A = B = 0.033 | | | $k$AB | 13 | | | | | (24) |
| | | | | | | | (i) | 2.7 | -2 | | | |
| | | | | | | | (f) | 1.5 | -3 | | | |
| .69 | $C_6H_5CH{:}C(COOH)_2 + Br_2$ | $CH_3COOH$ | A = 0.0125 | $HBr/Br_2$ = 1 - 4 | | $k$AB | 24 | 4.3 | -1 | | * | (13) |
| .70 | $C_6H_5C{:}C{:}COO^- + I_2$ | $H_2O$ | A = B = 0.010 | KI = 4 A = 4 B | | $k$AB | | | | | * | (12) |
| | | | | | | | 15.2 | 4.07 | -4 | | | |
| | | | | | | | 24.8 | 9.45 | -4 | | | |
| | | | | | | | 40.3 | 3.34 | -3 | | | |
| | | | | | | | 50.1 | 7.22 | -3 | | | |
| | | | | | | | 59.8 | 1.49 | -2 | 15.2 | | |
| | | | 0.025 | " | | " | 15.2 | 4.19 | -4 | | | " |
| | | | | | | | 24.8 | 1.04 | -3 | | | |
| | | | | | | | 40.3 | 3.63 | -3 | | | |
| | | | | | | | 50.1 | 7.49 | -3 | | | |
| | | | | | | | 59.8 | 1.58 | -2 | 15.2 | | |
| | | | 0.050 | " | | " | 15.2 | 4.74 | -4 | | | |
| | | | | | | | 24.8 | 1.14 | -3 | | | |
| | | | | | | | 40.3 | 3.78 | -3 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .70 | $C_6H_5C{:}C{:}COO^- + I_2$ *(continued)* | | | | | | 50.1 | 7.92 | -3 | | | |
| | | | | | | | 59.8 | 1.49 | -2 | 14.5 | | |
| | | | 0.094 | KI = 4 A = 4 B | | $k$AB | 15.2 | 6.01 | -4 | | | (12) |
| | | | | | | | 24.8 | 1.26 | -3 | | | |
| | | | | | | | 40.3 | 4.38 | -3 | | | |
| | | | | | | | 50.1 | 8.75 | -3 | 14.5 | | |
| .71 | *cis* - *o* - $CH_3OC_6H_4CH{:}CHCOOH + Br_2$ | $CCl_4$ | A = B = 0.033 | | | $k$AB | 13 | | | | | (24) |
| | | | | | | | (i) | 4.4 | -1 | | | |
| | | | | | | | (f) | 3.5 | -2 | | | |
| | | $CHCl_3$ | " | | | " | (i) | 5.1 | -1 | | | |
| | | | | | | | (f) | 4.0 | -1 | | | |
| .72 | *trans* - *o* - $CH_3OC_6H_4CH{:}CHCOOH + Br_2$ | $CHCl_3$ | A = B = 0.033 | | | $k$AB | 13 | | | | | (24) |
| | | | | | | | (i) | 3.0 | -1 | | | |
| | | | | | | | (f) | 2.8 | -2 | | | |
| .73 | *cis* - *o* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + BrCl$ | $CCl_4$ | $Br_2 = Cl_2$ | | | $k$AB | 0 | 1.4 | 0 | | | (8) |
| .74 | *trans* - *o* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + BrCl$ | $CCl_4$ | $Br_2 = Cl_2$ | | | $k$AB | 0 | 6.6 | -1 | | | (8) |
| .75 | *m* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + BrCl$ | $CCl_4$ | $Br_2 = Cl_2$ | | | $k$AB | 0 | 5.5 | -2 | | | (8) |
| .76 | *m* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + Br_2$ | $CCl_4$ | | | | $k$AB | 0 | ~ 3 | -4 | | | (8) |
| .77 | *o* - $NO_2C_6H_4CH{:}CHCOOH + Cl_2$ | $CH_3COOH$ | A = B = 0.05 | | | $k$AB | 24 | 1.83 | -5 | | | (10) |
| .78 | *m* - $NO_2C_6H_4CH{:}CHCOOH + Cl_2$ | $CH_3COOH$ | A = B = 0.05 | | | $k$AB | 24 | 1.83 | -4 | | | (10) |
| .79 | *p* - $NO_2C_6H_4CH{:}CHCOOH + Cl_2$ | $CH_3COOH$ | A = B = 0.05 | | | $k$AB | 24 | 8.2 | -5 | | | (10) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .80 | $m - NO_2C_6H_4CH{:}CHCOOH + Br_2$ | $CH_3COOH$ | A = B = 0.0125 | HBr | 0.0125 | $k$AB | 24 | 9.5 | -5 | | | (10) |
| .81 | $p - NO_2C_6H_4CH{:}CHCOOH + Br_2$ | $CH_3COOH$ | A = B = 0.0125 | HBr | 0.0125 | $k$AB | 24 | 5.5 | -5 | | | (10) |
| .82 | $o - NO_2C_6H_4CH{:}CHCOOCH_3 + Br_2$ | $CHCl_3$ | A = B = 0.033 | HBr | 0.015 | $k$AB | 24 | 1.35 | -5 | | | (10) |
| .83 | $m - NO_2C_6H_4CH{:}CHCOOCH_3 + Br_2$ | $CHCl_3$ | A = B = 0.033 | HBr | 0.015 | $k$AB | 24 | 1.26 | -4 | | | (10) |
| .84 | $p - NO_2C_6H_4CH{:}CHCOOCH_3 + Br_2$ | $CHCl_3$ | A = B = 0.033 | HBr | 0.015 | $k$AB | 24 | 6.8 | -5 | | | (10) |

## SUPPLEMENTARY TABLES

(.33) $CH_3CH{:}C(CH_3)COOH + Br_2$. *Solvent* $CH_3COOH$. *Temperature* 35.5 (1)

| A | B | Time(sec) for completion of 0.1 (fraction of complete reaction) | 0.5 |
|---|---|---|---|
| 0.033 | 0.017 | 3780 | 24600 |
| 0.017 | 0.033 | 10700 | 72000 |
| 0.033 | 0.009 | 8000 | 25200 |
| 0.017 | 0.009 | 10500 | 76500 |

No rate law established. Induction period observed.

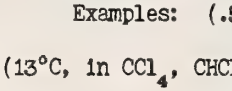
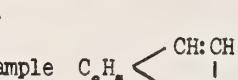
Classification of $Br_2$ addition reactions to a double bond ([24]):

(1) Rapid addition; some substitution; second-order $k$ increases with the progress of the reaction.

Examples: Reactions (.47) (.48) (.67) (.71) (.72).

(2) Slow addition; induction period; second-order $k$ decreases with the progress of the reaction.

Examples: (.57) (.61).

(3) No measurable addition (13°C, in $CCl_4$, $CHCl_3$). Example $C_6H_5$  ;  ; $C_6H_5CH{:}C(C_6H_5)CN$.

*Induction period* and *Fractional times* data in originals ([24]) ([9]). **Phenanthrene** derivatives + $Br_2$, see originals ([7]) ([8]).

## COMMENTS

**General.** In many instances, halogen addition reactions to multiple bonds present anomalies, the rates failing to follow satisfactorily a definite kinetic order. Indications of partial heterogeneity and of chain character, evidence by induction periods and sensitivity to inhibitors, are frequent. The mass-action laws given in the tables are very often purely conventional and do not establish a valid rate law of the reaction. Trends of the $k$, as defined, are illustrated by a statement of the fraction of the conversion, e.g. **(0.1)**, **(0.5)**, etc. to which the given value of $k$ refers, or by the symbols (i) = initial, (f) = final. The frequently observed catalysis by halogen ions $X^-$ is interpreted by ([17]) as $RCH{:}CHR + X^- \rightarrow RCHX - CHR$, followed by $RCHXCHR + X_2 \rightarrow RCHXCHXR + X^-$.

**References.** ([8]) BrCl formed from equimoleculer amounts of $Br_2$ and $Cl_2$. The data of $k$ are average values. Reactions of $o$ - $CH_3OC_6H_4CH{:}CBrCOOH$ and of $m$ - $CH_3OC_6H_4CH{:}CHCOOH$ with BrCl do not follow the second order. ([11]) Original $k$ converted from ml of 0.0182 $N$ $Na_2S_2O_3$ used for a 10-ml sample, and hours, to l $M^{-1}$ $sec^{-1}$ (GSF). For the bromides, $k_{n+1} / k_n \sim 18$, i.e. $k$ increases in a geometrical progression with increasing number of C atoms above 2 (for $CH_2{:}CHBr$, $n = 0$).
([13]) Data of $k$ given for 0.1 completion of the reaction.
([19]) ([24]) Unexplained serious discrepancies.

**Reactions.** **(.1)** Data of ([4]) refer to the lowest $k$ observed in dry $CCl_4$. According to ([23]) the reaction is autocatalyzed; rates are not reproducible, and no rate constant can be derived. Agreement between ([4]) and ([23])

## COMMENTS *(continued)*

on the fact that at the higher temperature (18°, 25°C) the reaction is considerably slower than at 0°C. HBr exerts an accelerating influence ([23]), contrary to ([4]). Assumption of $Br_2.H_2O$ as the brominating agent ([4]) contradicted by ([23]). (.2) In the gas phase ([25]) at 300°C, only an initial pressure drop is observed, coming to an early halt. Consequently, no reaction occurs on simple collision between A and B. (.7) The rate in $CH_3COOH$ is formulated by ([16]) $k_oA[I_3^-] + kAB + k'AB^3$, with only $k'$(initial) evaluated. The $I^-$ ions forming the $I_3^-$ are produced by a side reaction of A with the solvent ($CH_3COOH$). In $H_2O$, the formulation of the rate in the presence of $I^-$ ions added, is ([3]) $k_1A[I_3^-] + k_2AB$, with the equilibrium $I_2 + I^- \rightleftarrows I_3^-$. (.8) The total rate is represented by ([16]) as $k_oA[Br_3^-] + kAB + k'AB^2$, with the first term assuming increasing importance at higher temperatures; $k_o$ was not evaluated. The $Br^-$ ions forming $Br_3^-$ with $Br_2$ are produced by a side reaction of A with the solvent ($CH_3COOH$). Experimental evidence for acceleration by $Br^-$ is the 2.3-fold rate increase on addition of 0.004 HBr (at A = 0.008). Both $k$ and $k'$ show marked trends from initial (i) to final (f) values. The data do not establish the kinetics of the reaction. The orders of magnitude of the third-order rate constants of ([16]) and of ([18]) are in fair agreement; the figure of ([18]) at 50°C lies between the initial and the final $k'$ values of ([16]). Addition of 1 % $H_2O$ increases the rate by 80 % ([16]). Oxygen and $CO_2$ have no effect ([16]). In $CCl_4$, the reaction is partly heterogeneous ([18]), assumedly governed by the formation of a film on the wall of the reaction vessel; under these conditions, the reaction is *not* actually second-order, but rather more nearly first-order at 0° and 25°C, and more nearly third-order at 50°C. This accounts for the increase of the second-order $k$, at 0° and 25°C, from 0.2 and 0.6 completion of the reaction, and the abnormal decrease of the second-order $k$ with rising temperature.

(.9) The total rate in $CH_3COOH$ is represented ([16]) as $k_oA[I_3^-] + kAB + k'AB^3$, with only $k'$ evaluated. The $I^-$ ions forming $I_3^-$ are produced by a side reaction of A with the solvent ($CH_3COOH$). The data do not establish satisfactorily the kinetics of the reaction. Oxygen and $CO_2$ have no effect. (.11) In $CCl_4$, the reaction is partly heterogeneous. The data given are for $N_2$ atmosphere; $O_2$ inhibits, $H_2O$ accelerates the homogeneous part of the reaction which becomes predominant at lower concentrations. In $C_6H_5Cl$ and $CHCl_3$ the reaction is homogeneous; $k$ calculated from 0.5 time and 0.2 time,



942151 O—51——40

## COMMENTS *(continued)*

respectively, assuming second-order. In all cases, the rate tends to second-order with decreasing concentration. **(.12)** Reaction partly heterogeneous in $CCl_4$; at 0° and 25°C showing unimolecular, at 50°C termolecular character. **(.13)** The total rate in $CH_3COOH$ is represented ([16]) as $k_oA[Br_3^-] + kAB + k'AB^2$, with the first term small at 25°C but assuming increasing importance at higher temperatures; $k_o$ was not evaluated. The $Br^-$ ions forming $Br_3^-$ are produced by a side reaction of A with the solvent ($CH_3COOH$). Both $k$ and $k'$ show marked trends from initial (i) to final (f) values. The data do not establish satisfactorily the kinetics of the reaction. **(.20)** In $CH_3COOH$, second-order constants of ([13]) (at 0.1 completion of the reaction) are distinctly higher than the second-order $k$ of ([1]). In $CCl_4$, unexplained serious discrepancy between the second-order $k$ of ([19])([20]) and of ([24]). From the marked trends of both the second and third-order $k$ in $CH_3COOH$, between 0.1 and 0.5 completion of the reaction, the presence of an induction period, and the inhibition by $SbBr_3$, ([1]) concludes that the reaction involves a chain mechanism (no evidence for the specific mechanism proposed). **(.22)** The uninduced reaction (in the presence of HCl only) is unaffected by $O_2$. The reaction induced by $Fe^{++}$ is inhibited by $O_2$ and was carried out under $CO_2$. The inductor, $FeCl_2$ solution, is added to the A + B solution at the stated *rate R* (M/l per sec) and the reaction is allowed to proceed as long as the $Fe^{++}$ is being added (5 - 10 sec), then quenched immediately. The rate laws are different at low and at high B/A ratios. In the latter case, the rate depends on $R^{1/2}$. Further inductors, $Ti^{++}$, $V^{++}$, $V^{+++}$, $Mo^{+++}$, have the same effect as $Fe^{++}$; the reaction is also induced by $Ce^{++++}$. The reaction is inhibited by $Mn^{++}$, $Mo^{+++++}$, $VO^{++}$, $Cu^{++}$, $Co^{++}$, $Ce^{+++}$, $Pr^{+++}$, $Ni^{++}$, $Cr^{+++}$, $Fe^{+++}$, $La^{+++}$. Chain lengths, computed by $\Delta B/Rt$ (amount of $Cl_2$ consumed in the reaction divided by the total amount of inductor added during the same time) vary between 40 and 120. On the assumption that $R$ is identical with the rate of the very rapid initiating reaction (1) $Fe^{++} + Cl_2 \rightarrow FeCl^{++} + Cl$, followed by (2) $A + Cl \rightarrow COOHCHCl\dot{C}HCOOH$; (3) $COOHCHCl\dot{C}HCOOH + Cl_2 \rightarrow L + Cl$; (4) $COOHCHCl\dot{C}HCOOH + Cl \rightarrow L$; (5) $Cl + Cl \rightarrow Cl_2$; $k' = (k_2k_3/k_4)^{1/2}$, and $k'' = k_2/k_5^{1/2}$.

**(.23) (.24)** In $H_2O$ ([3]) the rate is $k_1AB + k_2A^-B$, with A = undissociated acid, $A^-$ = anion. The decrease of the rate with increasing $[Br^-]$ is due to the slower reaction of A (or $A^-$) with $Br_3^-$ as compared with the reaction with $Br_2$ (see .7). For the reaction in $CH_3COOH$ ([14]), $k' = k/K$,

## COMMENTS *(continued)*

with $K = [Br_2][Br^-]/[Br_3^-]$. Added salts exert retarding effects, in the order of decreasing effectiveness $NaBr > LiBr > CH_3COONa > LiSO_3C_2H_5 > LiSO_3C_6H_4CH_3$. At 50°C, 1 % $H_2O$ lowers $k$ by about 20 % for (.23), 75 % for (.24). (.46) Reaction partly heterogeneous in $CCl_4$; in $CH_3COOH$, only data of *E*. (.47) (.48) Unexplained serious discrepancy between data of ([19]) and ([24]).

(.52) Addition of $Br^-$ converts part of the $Br_2$ present into $Br_3^-$ which reacts with A much more slowly than $Br_2$ ($k_2 \sim 100k_1$). Consequently, $k$ decreases with increasing $[Br^-]$. With no $Br^-$ added in advance, some $Br_3^-$ is formed as a by-product of a side reaction, and causes $k$ within each single run to fall with the progress of the reaction much more rapidly than is warranted by a second-order law, on account of the progressive replacement of the more reactive $Br_2$ by the less reactive $Br_3^-$. Consequently, with no $Br^-$ added in advance, $k = k_2$ only at the initial stages of the reaction. The observed $k$ are rendered satisfactorily by the values of $k_1$, $k_2$, and the equilibrium constant $K = [Br_3^-]/[Br_2][Br^-] = 0.0024$. The primary step is represented as

$$A + B \rightarrow C_6H_5CH - CHC_6H_5 + Br^-.$$
$$\qquad\qquad\quad \vee$$
$$\qquad\qquad\quad Br^+$$

(.58) $k$ evaluated as second-order although the actual order is 2.9, i.e. closer to $kAB^2$. In $CCl_4$, the equilibrium $Br_2 + Cl_2 \rightleftharpoons 2\ BrCl$ is 60 % BrCl.

(.57) (.62) (.67) Unexplained serious discrepancy bewteen ([19]) and ([24]). (.70) The reaction proceeds actually between A and $I_3^-$, as, at $B > 0.005$, more than 90 % of it is present in the form of $I_3^-$ (with the stated amount of $I^-$ added). The increase of $k$ with the concentration of the reactants parallels the increasing stability of $I_3^-$. At $B < 0.0025$, $k$ increases rapidly with the dilution, which indicates increasing participation of a reaction between A and HIO (produced by hydrolysis of $I_2$). The total rate $-dB/dt = k_1A[I_3^-] + k_2A[HIO]$; $k_1 = k(K + [I^-])/[I^-]$; $K = [I_2][I^-]/[I_3^-]$. $k_2$ is not evaluated.

## LITERATURE

(1) S.V.Anantakrishnan, R.Venkataraman, *CSL* **1939**, 224. (2) P.D.Bartlett, D.S.Tarbell, *ACS* 1936, **58**, 466. (3) A.Berthoud, M.Mosset, *JCP* 1936, **33**, 272. (4) H.S.Davis, *ACS* 1928, **50**, 2769. (5) P.B.D.DeLaMare, R.A.Scott, R.W.Robertson, *CSL* **1945**, 509. (6) L.F.Fieser, C.C.Price, *ACS* 1936, **58**, 1834. (7) L.F.Fieser, C.C.Price, *ACS* 1936, **58**, 1838. (8) N.W.Hanson, T.C.James, *CSL* **1928**, 1955. (9) N.W.Hanson, D.M.Williams, *CSL* **1930**, 1059. (10) L.Hartmann, P.W.Robertson, *CSL* **1945**, 891.

(11) A.Juvala, Ber. 1930, **63**, 1989. (12) E.A.Moelwyn-Hughes, A.R.Legard, *CSL* **1933**, 424. (13) I.D.Morton, P.W.Robertson, *CSL* **1945**, 129. (14) K.Nozaki, R.A.Ogg, Jr., *ACS* 1942, **64**, 697. (15) K.Nozaki, R.A.Ogg, Jr., *ACS* 1942, **64**, 704. (16) K.Nozaki, R.A.Ogg, Jr., *ACS* 1942, **64**, 709. (17) R.A.Ogg, *ACS* 1935, **57**, 2727. (18) P.W.Robertson, N.T.Clare, K.J.McNaught, G.W.Paul, *CSL* **1937**, 335. (19) J.J.Sudborough, J.Thomas, *CSL* 1910, **97**, 715. (20) J.J.Sudborough, J.Thomas, *CSL* 1910, **97**, 2450.

(21) H.Taube, *ACS* 1943, **65**, 1876. (22) E.P.White, P.W.Robertson, *CSL* **1939**, 1509. (23) D.M.Williams, *CSL* **1932**, 2911. (24) D.M.Williams, T.C.James, *CSL* **1928**, 343. (25) D.M.Williams, *TFS* 1941, **37**, 749.

# ADDITION

## Ring opening by addition of $OH^-$

*Liquid phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $\underbrace{CH_2CH_2CH_2}CO + OH^- \rightarrow C_3H_7COO^-$ | $H_2O$ | 0.005 - 0.01 | $k$AB | 0 | 1.96 | -1 | | | |
| | | | | | 15 | 5.82 | -1 | 11.3 | 3.7 | 6 |
| .2 | $\underbrace{CH_2CH_2CH_2CH_2}CO + OH^- \rightarrow C_4H_9COO^-$ | $H_2O$ | 0.005 - 0.01 | $k$AB | 0 | 8.23 | -2 | | | |
| | | | | | 15 | 2.40 | -1 | | | |
| | | | | | 25 | 4.68 | -1 | 11.2 | 1.3 | 6 |
| | | $H_2O + C_2H_5OH$ 21 % | " | " | 0 | 6.31 | -2 | | | |
| | | | | | 15 | 1.82 | -1 | | | |
| | | | | | 25 | 3.43 | -1 | 10.8 | 4.8 | 5 |
| | | $H_2O + C_2H_5OH$ 40 % | " | " | 0 | 3.0 | -2 | | | |
| | | | | | 15 | 1.01 | -1 | | | |
| | | | | | 25 | 2.06 | -1 | 12.6 | 6.2 | 6 |
| | | $H_2O + C_2H_5OH$ 60 % | " | " | 0 | 1.45 | -2 | | | |
| | | | | | 15 | 6.10 | -2 | | | |
| | | | | | 25 | 1.38 | -1 | 14.5 | 1.0 | 8 |
| .3 | $\underbrace{C_6H_4COOCH_2} + OH^- \rightarrow C_6H_5COOCH_2O^-$ | $H_2O$ | 0.005 - 0.01 | $k$AB | 0 | 3.92 | -2 | | | |
| | | | | | 15 | 1.29 | -1 | | | |
| | | | | | 25 | 2.73 | -1 | 12.6 | 8.0 | 6 |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $C_6H_4COOCH_2 + OH^- \rightarrow C_6H_5COOCH_2O^-$ *(continued)* | $H_2O + C_2H_5OH$ 21.5 % | 0.005 - 0.01 | $k$AB | 0 | 2.06 | -2 | | | |
| | | | | | 15 | 7.38 | -2 | | | |
| | | | | | 25 | 1.57 | -1 | 13.2 | 1.3 | 7 |
| | | $H_2O + C_2H_5OH$ 40 % | " | " | 0 | 8.84 | -3 | | | |
| | | | | | 15 | 3.78 | -2 | | | |
| | | | | | 25 | 8.84 | -2 | 14.9 | 1.3 | 8 |
| | | $H_2O + C_2H_5OH$ 60 % | " | " | 0 | 4.32 | -3 | | | |
| | | | | | 15 | 2.12 | -2 | | | |
| | | | | | 25 | 5.18 | -2 | 16.1 | 5.7 | 8 |
| .4 | $5\text{-}NH_2C_6H_3COOCH_2 + OH^- \rightarrow NH_2C_6H_4COOCH_2O^-$ | $H_2O$ | " | " | 0 | 2.27 | -2 | | | |
| | | | | | 15 | 8.16 | -2 | | | |
| | | | | | 25 | 1.76 | -1 | 13.3 | 1.7 | 8 |

## COMMENTS

Electric conductivity measurements.

## LITERATURE

D. S. Hegan, J. H. Wolfenden, *CSL* **1939**, 508.

# OXIDATIVE ADDITION

## C oxide + halogen

Rate measured $-\Delta p$



Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $CO + Cl_2 \rightarrow COCl_2$ | $k\,AB^{3/2}$ | 349 | 3.81 | 0 | | | | (1) |
| | | | 395 | 1.55 | + 1 | | | | |
| | | | 452 | 7.78 | + 1 | 11.5 | 1.45 | 10 | |

## COMMENTS

Reverse reaction, see 541.470. The proposed mechanism, $Cl_2 \rightleftarrows 2\,Cl$; $Cl + CO \rightleftarrows COCl$; $COCl + Cl_2 \rightarrow COCl_2 + Cl$; is based on analogy with photochemical reactions which seem to rule out $Cl_3$ as intermediate (2).

## LITERATURE

(1) M. Bodenstein, H. Plaut, *ZPC* 1924, **110**, 399.
(2) M. Bodenstein, W. Brenschede, H.J. Schumacher, *ZPC*[B] 1935, **28**, 81; 1938, **40**, 121.

# OXIDATIVE ADDITION

## N oxides



Rate measured $-\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|
| .1 | $2\ NO + O_2 \rightarrow 2\ NO_2$ | $A + B = 3 \times 10^{-5} - 7 \times 10^{-4}$ | $k A^2B$ | −130 | 1.48 | +5 | (9) |
| | | | | −78 | 2.58 | +4 | " |
| | | | | −19 | 1.31 | +4 | " |
| | | | | 0 | 1.04 | +4 | " |
| | | | | 60 | 5.5 | +3 | (1) (4) |
| | | | | 141 | 4.0 | +3 | " |
| | | | | 241 | 3.0 | +3 | " |
| | | | | 340 | 2.8 | +3 | " |
| | | | | 389 | 2.5 | +3 | " |

## COMMENTS

Selected data. The rate is unaffected by added $H_2O$, $NO_2$, $SO_2$ ([4]), $N_2$ ([10]), increased surface ([4]), magnetic field ([8]). Homogeneity, confirmed by ([6]), contested by ([12]). Proposed mechanisms: ([3]) $2\ NO \rightleftarrows (NO)_2$; $(NO)_2 + O_2 \rightarrow 2\ NO_2$; ([13]) $NO + O_2 \rightleftarrows NO_3$; $NO_3 + NO \rightarrow 2\ NO_2$. The negative temperature coefficient is attributed by ([7]) to suppression of translation and rotation in reactants and replacement as vibration in complex, requiring no activation energy.

**Reverse reaction.** $2\ NO_2 \rightarrow 2\ NO + O_2$, rate = $k\,AB$; $k$ can be calculated from the rate of the forward reaction and the equilibrium constant ([2]) $\log K_p = -(2891/T) + 1.75 \log T + 0.0046\,T - 8.92 \times 10^{-6}T^2 + 3.934$ (in atm.).

## LITERATURE

([1]) M. Bodenstein, *ZEC* 1918, **24**, 183; *ZAC* 1918, **31**, 145. ([2]) M. Bodenstein, *ZPC* 1932, **100**, 75. ([3]) M. Bodenstein, *HCA* 1935, **18**, 743. ([4]) M. Bodenstein, L. Wachenheim, *ZPC* 1922, **100**, 87. ([5]) E. Briner, W. Pfeiffer, G. Malet, *JCC* 1924, **21**, 25. ([6]) M. S. Furman, *ZhFKh* 1944, **18**, 385. ([7]) H. Gershinovitz, Eyring, *ACS* 1935, **57**, 985. ([8]) G. Kornfeld, E. K. Klinger, *ZPC*[B] 1932, **4**, 37. ([9]) F. Matthes, *Thesis*, Berlin 1933. ([10]) D. Porret, *Thesis*, Berlin 1937. ([11]) F. Raschig, *ZAC* 1915, **18**, 1281. ([12]) E. M. Stoddart, *CSL* **1939**, 5. ([13]) M. Trautz, *ZEC* 1916, **22**, 104.

# OXIDATIVE ADDITION

## N oxide + halogen

*Gas phase*

Rate measured $-\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ NO + Cl_2 \rightarrow 2\ NOCl$ | A = 0.001 - 0.004 | $kA^2B$ | 0 | 5.4 | 0 | | * | (3) |
| | | B = 0.0004 - 0.005 | | 30 | 1.25 | +1 | | | |
| | | | | 59 | 2.48 | +1 | | | |
| | | | | 150 | 1.05 | +2 | | | |
| | | | | 197 | 1.91 | +2 | 4.5 | | |
| | | 0.01 - 0.015 | $kA^2B(1-\sigma)$; $d\sigma/dt = k'(1-\sigma)L$ | | | | | * | (4) |
| | | | $k$ | 15 | 5.70 | 0 | | | |
| | | | " | " | 1.18* | 0 | | | |
| | | | " | 25 | 6.90 | 0 | | | |
| | | | " | " | 2.59* | 0 | | | |
| | | | $k_2$ | 15 - 25 | 5.6 | -2 | | | |
| .2 | $2\ NO + Br_2 \rightarrow 2\ NOBr$ | 0.0003 - 0.002 | $kA^2B$ | -8.2 | 2.12 | +3 | | * | (2) |
| | | | | 0 | 2.35 | +3 | | | |
| | | | | 15 | 2.67 | +3 | 1.5 | | |

## COMMENTS

(.1) Data from ([3]), in substantial agreement with earlier data of ([5]). Mechanism proposed ([1]) $2\ NO \rightleftarrows (NO)_2$; $(NO)_2 + Cl_2 \rightarrow 2\ NOCl$; ([5]) $NO + Cl_2 \rightleftarrows NOCl_2$; $NOCl_2 + NO \rightarrow 2\ NOCl$; no evidence for either. Data of ([4]); The rate is represented by $kA^2B(1-\sigma)$, where $\sigma$ = fraction of surface covered; in $d\sigma/dt = k'(1-\sigma)L$, the constant $k'$ is independent of the temperature. Starred (*) values of $k$ refer to rates observed on surface poisoned after many runs, when reproducible rates from run to run and concordant values within one run are found. Intense drying with $P_2O_5$ gave, at 15 and 25°C, $k$ = 5.86 and 7.25; these are taken to correspond to rates on NOCl-free surface; the reaction is inhibited by adsorbed NOCl on moist surface. Data of ([3]), extrapolated to 15° and 25°C, give $k$ = 8.19 and 10.9, as against ([4]) 5.70 (1.18*) and 6.90 (2.59*), i.e. distinctly higher than ([4]). (.2) Selected data. Proposed mechanisms of ([1]) and ([5]), as for reaction (.1); neither mechanism substantiated.

**Reverse reaction** $2\ NOBr \rightarrow 2\ NO + Br_2$, rate = $kAB$; $k$ can be calculated from the forward reaction and the equilibrium constant ([5]) $\log K_p = (-2867/T) + 8.025$ (in atm.).

## LITERATURE

([1]) M. Bodenstein, *HCA* 1935, **18**, 743. ([2]) W. Krauss, *ZPC*[A] 1936, **175**, 295. ([3]) W. Krauss, M. Saracini, *ZPC*[A] 1937, **178**, 245. ([4]) E. Stoddart, *CSL* **1940**, 823; **1944**, 388. ([5]) M. Trautz, *ZEC* 1916, **22**, 104; M. Trautz, Dalal, *ZAC* 1918, **102**, 149; 1920, **110**, 1.

# ADDITION

## Alkyl halide + aliphatic amine

## Quaternary base formation

*Gas phase*

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|
| .1 | $C_2H_5I + (C_2H_5)_3N$ | 100 A = 1.0 ; 100 B = 1.0 | $k$AB | 140.6 | 1.9 | -4 |
| | | 2.74 1.70 | | " | 3.68 | -4 |
| | | 4.70 2.90 | | " | 6.46 | -4 |
| | | 2.11 4.37 | | " | 1.31 | -3 |
| | | 7.91 13.6 | | " | 1.86 | -3 |
| | | 11.2 15.4 | | " | 2.67 | -3 |

## COMMENTS

Selected figures. The second-order $k$ increases with increasing initial amounts of reactants. The reaction is clearly partly heterogeneous, as evidenced by the strong rate-increasing effect of packing. The gas-phase reaction is ~ 5 times as fast as in $C_6H_{14}$, and somewhat slower than in $CCl_4$.

## LITERATURE

E. A. Moelwyn-Hughes, C. N. Hinshelwood, *CSL* **1932**, 230.

# ADDITION

## Aliphatic carboxylic acid ester + Amine

## Quaternary base formation

*Liquid phase*

Reaction type $RCOOR' + NR''_3 \longrightarrow RCOO^- + NR''_3R'^+$

Amounts are in M/l. Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $CH_3COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 1.65 | -6 |
| .2 | $CH_3CHOHCOOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 9.74 | -6 |

## COMMENTS

$\log k = -2.46 + 0.67 \log K$ (ionization constant of the acid).

## LITERATURE

L. P. Hammett, H. L. Pfluger, *ACS* 1933, 55, 4079.

# ADDITION

## Aromatic carboxylic acid ester + Amine

*Liquid phase*

## Quaternary base formation

Amounts are in M/l. Rates are in M/l per sec.

Reaction type $ArCOOR + NR''_3 \rightarrow ArCOO^- + NR''_3R^+$

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 4.48 | -6 |
| .2 | $C_6H_4(COOCH_3)_2 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 3.45 | -5 |
| .3 | $o - CH_3C_6H_4COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 4.62 | -6 |
| .4 | $p - CH_3C_6H_4COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 3.41 | -6 |
| .5 | $o - NO_2C_6H_4COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | (9.15) | -5 |
| .6 | $p - NO_2C_6H_4COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 3.14 | -5 |
| .7 | $o - ClC_6H_4COOCH_3 + N(CH_3)_3$ | $CH_3OH$ | A = 0.14 - 0.62; B ~ 0.18 | $k$AB | 100 | 2.03 | -5 |

### COMMENTS

$\log k = -2.46 + 0.67\,K$ (ionization constant of the acid). (.5) extrapolated to zero time.

### LITERATURE

L. P. Hammett, H. L. Pfluger, *ACS* 1933, 55, 4079.



942151 O—51——41

# ADDITION

## Alkyl halide + aliphatic amine
## Quaternary base formation

*Liquid phase*

Reaction type $RX + NR'_3 \rightarrow R'_3\,NR^+ + X^-$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3I + N(CH_3)_3$ | $C_6H_6$ | A = B = 0.1 | $k$ AB | 4.4 | 6.0 | -3 | | | | | ([3]) |
| | | | | | 16.0 | 1.15 | -2 | | | | | |
| | | | | | 25.0 | 1.85 | -2 | | | | | |
| | | | | | 40.1 | 3.71 | -2 | 8.7 | | | | |
| .2 | $CH_3I + N(C_2H_5)_3$ | $C_6H_6$ | A = B = 0.1 | $k$ AB | 4.6 | 4.4 | -4 | | | | * | ([2]) |
| | | | | | 14 | 8.0 | -4 | | | | ([2a]) | ([3]) |
| | | | | | 25.0 | 1.45 | -3 | | | | | |
| | | | | | 40.0 | 3.20 | -3 | | | | | |
| | | | | | 60 | 8.25 | -3 | 9.7 | 2.1 | 4 | | ([2a]) |
| | | $C_6H_5NO_2$ 25% + $C_6H_6$ 75% | | $k$ AB | 4.4 | 2.20 | -3 | | | | | ([2a]) |
| | | | | | 15 | 4.3 | -3 | | | | | |
| | | | | | 25.0 | 7.75 | -3 | | | | | |
| | | | | | 40.0 | 1.55 | -2 | 9.5 | 7.7 | 4 | | |
| | | $C_6H_5NO_2$ 50% + $C_6H_6$ 50% | | $k$ AB | 4.6 | 4.4 | -3 | | | | | ([2a]) |
| | | | | | 15 | 8.0 | -3 | | | | | |
| | | | | | 25.0 | 1.48 | -2 | | | | | |
| | | | | | 40.1 | 3.41 | -2 | 9.8 | 2.4 | 5 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3I + N(C_2H_5)_3$ *(continued)* | $C_6H_5NO_2$ 75% + $C_6H_6$ 25% | | $k$ AB | 4.7 | 7.0 | -3 | | | | | [2a] |
| | | | | | 15 | 1.30 | -2 | | | | | |
| | | | | | 25.0 | 2.44 | -2 | | | | | |
| | | | | | 40.0 | 5.50 | -2 | 10.0 | 5.8 | 5 | | |
| | | $C_6H_5NO_2$ 90% + $C_6H_6$ 10% | | $k$ AB | 4 | 9.27 | -3 | | | | | [2a] |
| | | | | | 15 | 1.79 | -2 | | | | | |
| | | | | | 25 | 3.21 | -2 | | | | | |
| | | | | | 40 | 7.08 | -2 | 9.8 | 5.0 | 5 | | |
| | | $C_6H_5NO_2$ | | $k$ AB | 4.1 | 9.35 | -3 | | | | | [2] |
| | | | | | 5 | 1.07 | -2 | | | | | [2a] |
| | | | | | 15.0 | 1.9 | -2 | | | | [2] | [2a] |
| | | | | | 25.0 | 3.35 | -2 | | | | " | " |
| | | | | | 40.0 | 7.3 | -2 | 9.7 | 4.3 | 5 | " | " |
| .3 | $C_2H_5Cl + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = 1.43; B = 0.14 | $k$ AB | 55 | 4.86 | -5 | | | | | [1] |
| .4 | $C_2H_5I + N(CH_3)_3$ | $C_6H_6$ | A = B = 0.1 | $k$ AB | 25.0 | 2.12 | -4 | | | | | [3] |
| | | | | | 40.1 | 5.26 | -4 | | | | | |
| | | | | | 80.6 | 4.39 | -3 | 11.4 | | | | |
| .5 | $C_3H_7Br + N(CH_3)_3$ | $C_6H_6$ | A = B = 0.1 | $k$ AB | 80.5 | 1.78 | -4 | | | | | [3] |
| | | | | | 99.7 | 4.26 | -4 | | | | | |
| | | | | | 117.6 | 8.76 | -4 | | | | | |
| | | | | | 139.4 | 1.96 | -3 | 11.7 | | | | |
| .6 | $C_3H_7I + N(CH_3)_3$ | $C_6H_6$ | A = B = 0.1 | $k$ AB | 40.0 | 1.20 | -4 | | | | | [3] |
| | | | | | 80.6 | 9.95 | -4 | | | | | |
| | | | | | 99.7 | 2.19 | -3 | 11.2 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .7 | $(CH_3)_2CHI + N(C_2H_5)_3$ | $C_6H_6$ | A = B = 0.1 | $k$ AB | 99.6 | 1.77 | -6 | | | | * | (2) |
| | | | | | 120.4 | 6.25 | -6 | | | | (2) | (2a) |
| | | | | | 138 | 1.45 | -6 | | | | " | " |
| | | | | | 153 | 2.9 | -6 | 17.1 | 1.9 | 4 | | (2) |
| | | | | | | | | 16.3 | 7.7 | 3 | | (2a) |
| | | $C_6H_5NO_2$ 25 % + $C_6H_6$ 75 % | | $k$ AB | 99.8 | 1.51 | -5 | | | | | (2a) |
| | | | | | 120.6 | 4.59 | -5 | | | | | |
| | | | | | 139.0 | 1.02 | -4 | | | | | |
| | | | | | 153.4 | 2.21 | -4 | 16.5 | 1.2 | 4 | | |
| | | $C_6H_5NO_2$ 50 % + $C_6H_6$ 50 % | | $k$ AB | 80.2 | 1.68 | -5 | | | | | (2a) |
| | | | | | 99.9 | 5.62 | -5 | | | | | |
| | | | | | 120 | 1.96 | -4 | | | | | |
| | | | | | 153.4 | 8.23 | -4 | 16.0 | 1.6 | 5 | | |
| | | $C_6H_5NO_2$ 75 % + $C_6H_6$ 25 % | | $k$ AB | 99 | 1.23 | -4 | | | | | (2a) |
| | | | | | 121 | 4.17 | -4 | | | | | |
| | | | | | 153 | 2.05 | -3 | 16.1 | 3.9 | 5 | | |
| | | $C_6H_5NO_2$ | A = B = 0.1 | $k$ AB | 60.1 | 1.95 | -5 | | | | | (2) |
| | | | | | 80.0 | 8.22 | -5 | | | | (2) | (2a) |
| | | | | | 100 | 2.9 | -4 | | | | " | " |
| | | | | | 120 | 8.8 | -4 | 16.0 | 6 | 5 | " | " |
| | | " | A = B = 0.04 | " | 79.9 | 9.47 | -5 | | | | | (2) |
| | | | | | 100.2 | 3.08 | -4 | | | | | |
| | | | | | 121.1 | 9.00 | -4 | | | | | |
| | | " | A = B = 0.02 | " | 121.1 | 1.10 | -3 | | | | | (2) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .8 | $CH_2Cl_2 + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = 1.43; B = 0.143 | $k$ AB | 55 | 1.01 | -5 | | | | | (1) |
| .9 | $CH_2Br_2 + N(CH_3)_3$ | $(CH_3)_3CO$ 90 % | A = 0.07; B = 0.15 | $k$ AB | 35 | 7.0 | -5 | | | | | (1) |
| | | | 1.47 0.146 | | 45 | 1.23 | -4 | | | | | |
| | | | 0.113 0.113 | | " | 1.56 | -4 | | | | | |
| | | | 0.141 0.141 | | 55 | 3.50 | -4 | | | | | |
| .10 | $CH_2ClCH_2Cl + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = 1.43; B = 0.143 | $k$ AB | 55 | 4.65 | -6 | | | | | (1) |
| .11 | $CH_2BrCH_2Br + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = 1.47; B = 0.147 | $k$ AB | 35 | 5.80 | -5 | | | | | (1) |
| | | | 0.087 0.087 | | " | 9.30 | -5 | | | | | |
| | | | 0.075 0.150 | | " | 9.30 | -5 | | | | | |
| | | | 1.46 0.146 | | 45 | 1.30 | -4 | | | | | |
| | | | 0.147 0.147 | | " | 1.78 | -4 | | | | | |
| | | | 0.229 0.114 | | 55 | 3.30 | -4 | | | | | |
| | | | 0.071 0.071 | | " | 3.82 | -4 | | | | | |
| | | | 1.83 0.176 | | " | 2.18 | -4 | | | | | |
| .12 | $CH_2BrCH_2CH_2Br + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = 0.12; B = 0.145 | $k$ AB | 35 | ~ 6.5 | -4 | | | | | (1) |
| | | | 0.23 0.115 | | " | 4.66 | -4 | | | | | |
| | | | 1.46 0.146 | | 45 | 7.36 | -4 | | | | | |
| | | | 0.226 0.113 | | " | 1.00 | -3 | | | | | |
| | | | 0.223 0.111 | | 55 | 1.92 | -3 | | | | | |
| .13 | $BrN(CH_3)_3CH_2Br + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = B = 0.107 | $k$ AB | 55 | 5.3 | -5 | | | | | (1) |
| .14 | $BrN(CH_3)_3CH_2CH_2Br + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = 0.085; B = 0.1 | $k$ AB | 35 | 1.0 | -5 | | | | | (1) |
| | | | | | 55 | 5.7 | -5 | | | | | |
| .15 | $BrN(CH_3)_3CH_2CH_2CH_2Br + N(CH_3)_3$ | $(CH_3)_2CO$ 90 % | A = B = 0.11 | $k$ AB | 35 | 4.0 | -4 | | | | | (1) |
| | | | | | 55 | 1.4 | -3 | | | | | |

## COMMENTS

**(.2)** Averaged close data of ([2]) ([2a]) and ([3]) are underlined. **(.7)** In $C_6H_6$, pronounced autocatalysis, attributed to increasing polarity of the solvent through dissolved quaternary salt.

## LITERATURE

([1]) W.C.Davies, E.B.Evans, F.L.Hulbert, *CSL* **1939**, 412.

([2]) K. J. Laidler, C. N. Hinshelwood, *CSL* **1938**, 858.

([2a]) H. C. Raine, C. N. Hinshelwood, *CSL* **1939**, 1378.

([3]) C. A. Winkler, C. N. Hinshelwood, *CSL* **1935**, 1147.

# ADDITION

## Alkyl halide + aromatic amine → quaternary base

*Liquid phase*

Reaction type $RX + ArNR'R'' \rightarrow ArNRR'R''^{+} + X^{-}$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^{o} \times 10^{n}$ $k^{o}$ | $n$ | $E$ | $A = A^{o} \times 10^{n}$ $A^{o}$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3I + C_6H_5N(CH_3)_2$ | $CH_3OH$ | | $k$ AB | 25 | 5.62 | -5 | | | | | (2) |
| | | | | | 35.5 | 1.31 | -4 | | | | | |
| | | | | | 65 | 1.19 | -3 | 15.2 | 7.9 | 6 | | |
| | | $C_6H_5NO_2$ | A = B = 0.05 | $k$ AB | 24.8 | 8.39 | -5 | | | | | (2a) |
| | | | | | 40.1 | 2.10 | -4 | | | | | |
| | | | | | 60.0 | 7.72 | -4 | 12.8 | 2.2 | 5 | | |
| .2 | $CH_3I + C_6H_5N(CH_3)(C_2H_5)$ | $CH_3OH$ | | $k$ AB | 44.8 | 1.97 | -4 | | | | | (2) |
| | | | | | 65.1 | 8.50 | -4 | | | | | |
| | | | | | 84.2 | 2.90 | -3 | 15.4 | 7.9 | 6 | | |
| .3 | $CH_3I + C_6H_5N(C_2H_5)_2$ | $CH_3OH$ | | $k$ AB | 65 | 1.24 | -4 | | | | | (2) |
| | | | | | 85.5 | 5.69 | -4 | | | | | |
| | | | | | 99.4 | 1.49 | -3 | 18.0 | 5 | 7 | | |
| .4 | $CH_3I + C_6H_5N(CH_3)(C_3H_7)$ | $CH_3OH$ | | $k$ AB | 44.8 | 1.12 | -4 | | | | | (2) |
| | | | | | 65.2 | 4.94 | -4 | | | | | |
| | | | | | 84.9 | 1.75 | -3 | 15.4 | 5 | 6 | | |
| .5 | $CH_3I + C_6H_5N(C_2H_5)(C_3H_7)$ | $CH_3OH$ | | $k$ AB | 65.0 | 7.75 | -5 | | | | * | (2) |
| | | | | | 84.3 | 3.54 | -4 | | | | | |
| | | | | | 99.8 | 1.10 | -3 | 19.0 | 1.6 | 8 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $CH_3I + C_6H_5N(C_3H_7)_2$ | $CH_3OH$ | | $k$ AB | 65.2 | 5.48 | -5 | | | | * | (2) |
| | | | | | 84.7 | 2.52 | -4 | | | | | |
| | | | | | 100 | 7.72 | -4 | 19.0 | 1.2 | 8 | | |
| .7 | $CH_3I + C_6H_5N(C_4H_9)_2$ | $CH_3OH$ | | $k$ AB | 65 | 6.80 | -5 | | | | | (2) |
| | | | | | 85 | 2.83 | -4 | | | | | |
| | | | | | 100 | 8.66 | -4 | 19.0 | 1.2 | 8 | | |
| .8 | $CH_3I + m\text{-}CH_3C_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 35.5 | 1.75 | -4 | | | | | (1a) |
| | | | | | 45.0 | 3.74 | -4 | | | | | |
| | | | | | 55.0 | 7.56 | -4 | | | | | |
| | | | | | 65.0 | 1.50 | -3 | 14.9 | 6.3 | 6 | | |
| .9 | $CH_3I + p\text{-}CH_3C_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 25.0 | 1.42 | -4 | | | | | (1a) |
| | | | | | 35.0 | 3.2 | -4 | | | | | |
| | | | | | 50.0 | 9.4 | -4 | | | | | |
| | | | | | 65.0 | 3.55 | -3 | 14.5 | | | | |
| | | $C_6H_5NO_2$ | A = B = 0.05 | $k$ AB | 24.8 | 2.84 | -4 | | | | | (2a) |
| | | | | | 40.1 | 7.96 | -4 | | | | | |
| | | | | | 60.0 | 2.53 | -3 | 12.3 | 3.3 | 5 | | |
| .10 | $CH_3I + p\text{-}CH_3OC_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 25.0 | 2.53 | -5 | | | | | (1a) |
| | | | | | 35.0 | 5.72 | -4 | | | | | |
| | | | | | 45.0 | 1.14 | -3 | | | | | |
| | | | | | 55.0 | 2.34 | -3 | 14.3 | 7.9 | 6 | | |
| | | $C_6H_5NO_2$ | A = B = 0.05 | $k$ AB | 15 | 3.46 | -4 | | | | | (2a) |
| | | | | | 24.8 | 7.19 | -4 | | | | | |
| | | | | | 40.1 | 1.83 | -3 | | | | | |
| | | | | | 60.0 | 5.60 | -3 | 11.7 | 2.8 | 5 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .11 | $CH_3I + o\text{-}C_6H_5C_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 65 | 3.0 | -5 | | | | | ([1a]) |
| | | | | | 85.9 | 1.99 | -4 | | | | | |
| | | | | | 101 | 6.74 | -4 | 21.6 | 3 | | | |
| .11.1 | $CH_3I + p\text{-}C_6H_5C_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 45 | 4.96 | -5 | | | | | ([1a]) |
| | | | | | 55 | 9.29 | -5 | 15.4 | 5 | 7 | | |
| .12 | $CH_3I + o\text{-}C_6H_5OC_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 35 | 7.14 | -5 | | | | | ([1a]) |
| | | | | | 45 | 1.60 | -4 | | | | | |
| | | | | | 55 | 3.57 | -4 | | | | | |
| | | | | | 65 | 7.47 | -4 | 16.2 | 2.5 | 7 | | |
| .13 | $CH_3I + o\text{-}NO_2C_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 135 | 2.15 | -4 | | | | | ([1a]) |
| | | | | | 145.1 | 4.01 | -4 | 20.9 | 5 | 7 | | |
| .14 | $CH_3I + o\text{-}FC_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 45 | 7.10 | -5 | | | | | ([1a]) |
| | | | | | 55 | 1.50 | -4 | | | | | |
| | | | | | 65 | 3.09 | -4 | | | | | |
| | | | | | 74.8 | 5.95 | -4 | 16.3 | 1 | 7 | | |
| .15 | $CH_3I + p\text{-}FC_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 35 | 1.06 | -4 | | | | | ([1a]) |
| | | | | | 45 | 2.32 | -4 | | | | | |
| | | | | | 55 | 4.95 | -4 | | | | | |
| | | | | | 65 | 9.63 | -4 | 15.5 | 1 | 7 | | |
| .16 | $CH_3I + o\text{-}ClC_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 75 | 1.02 | -4 | | | | | ([1a]) |
| | | | | | 85.2 | 2.33 | -4 | | | | | |
| | | | | | 98.9 | 6.53 | -4 | 19.9 | 3.1 | 8 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .17 | $CH_3I + p\text{-}ClC_6H_4N(CH_3)_2$ | $CH_3OH$ | A = B = 0.1 | $k$ AB | 45 | 7.87 | -5 | | | | | ([1a]) |
| | | | | | 55 | 1.70 | -4 | | | | | |
| | | | | | 65 | 3.5 | -4 | | | | | |
| | | | | | 75 | 7.2 | -4 | 16.2 | 1 | 7 | | |
| | | $C_6H_5NO_2$ | A = B = 0.05 | $k$ AB | 15.0 | 9.26 | -6 | | | | | ([2a]) |
| | | | | | 24.8 | 2.11 | -5 | | | | | |
| | | | | | 40.1 | 5.97 | -5 | | | | | |
| | | | | | 60.0 | 2.56 | -4 | 13.9 | 3.9 | 5 | | |
| .18 | $CH_3I + p\text{-}BrC_6H_4N(CH_3)_2$ | $C_6H_5NO_2$ | A = B = 0.1 | $k$ AB | 15.0 | 8.24 | -6 | | | | | ([2a]) |
| | | | | | 24.8 | 1.80 | -5 | | | | | |
| | | | | | 40.1 | 5.54 | -5 | | | | | |
| | | | | | 60.1 | 2.13 | -4 | 13.7 | 2.2 | 5 | | |
| | **Aryl - substituted alkyl halide** | | | | | | | | | | | |
| .19 | $C_6H_5CH_2Cl + C_6H_5NH_2$ | $CH_3OH$ | A = 0.05; B = 0.2 | $k$ AB | 30 | 3.96 | -5 | | | | | ([3]) |
| | | | 0.01 0.4 | | 35 | 7.60 | -5 | | | | | |
| | | | " " | | 45 | 1.71 | -4 | | | | | |
| | | | 0.05 0.2 | | 50 | 2.20 | -4 | | | | | |
| | | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 1.16 | -5 | | | | * | ([1]) |
| .20 | $C_6H_5CH_2Cl + C_6H_5NHC_2H_5$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 5.65 | -5 | | | | * | ([3]) |
| | | | 0.4 0.1 | | 35 | 9.60 | -5 | | | | | |
| | | | " " | | 45 | 2.15 | -4 | | | | | |
| | | | 0.2 0.05 | | 50 | 2.95 | -4 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .21 | $C_6H_5CH_2Cl + C_6H_5N(CH_3)_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 3.70 | -5 | | | | * | ([3]) |
| | | | 0.4 0.1 | | 35 | 5.80 | -5 | | | | | |
| | | | " " | | 45 | 1.34 | -4 | | | | | |
| | | | 0.2 0.05 | | 50 | 1.87 | -4 | | | | | |
| .22 | $C_6H_5CH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 5.80 | -4 | | | | * | ([1]) |
| .23 | $C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH_2$ | $(CH_3)_2CO$ | | $k$ AB | 35 | 6.2 | -5 | | | | | ([4]) |
| | | | | | 45 | 1.24 | -4 | 13.6 | | | | |
| .24 | $C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(m\text{-}C_6H_4CH_3)$ | $(CH_3)_2CO$ | | $k$ AB | 45 | 1.95 | -5 | | | | | ([4]) |
| .25 | $C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(p\text{-}C_6H_4CH_3)$ | $(CH_3)_2CO$ | | $k$ AB | 45 | 2.83 | -5 | | | | | ([4]) |
| .26 | $C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(m\text{-}C_6H_4Cl)$ | $(CH_3)_2CO$ | | $k$ AB | 45 | 2.33 | -6 | | | | | ([4]) |
| .27 | $C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(p\text{-}C_6H_4Cl)$ | $(CH_3)_2CO$ | | $k$ AB | 45 | 3.00 | -6 | | | | | ([4]) |
| .28 | $C_6H_5CH_2Br + p\text{-}NO_2C_6H_4NH_2$ | $(CH_3)_2CO$ | | $k$ AB | 35 | 6.0 | -5 | | | | | ([4]) |
| | | | | | 45 | 1.22 | -5 | 13.6 | | | | |
| .29 | $C_6H_5CH_2Br + p\text{-}NO_2C_6H_4CH_2NHC_6H_5$ | $(CH_3)_2CO$ | | $k$ AB | 35 | 1.17 | -4 | | | | | ([4]) |
| | | | | | 45 | 2.33 | -4 | | | | | |
| .30 | $C_6H_5CH_2Br + p\text{-}NO_2C_6H_4CH_2NH(p\text{-}C_6H_4CH_3)$ | $(CH_3)_2CO$ | | $k$ AB | 45 | ~ 2.5 | -5 | | | | | ([4]) |
| .31 | $C_6H_5CH_2Br + p\text{-}NO_2C_6H_4CH_2NH(p\text{-}C_6H_4Cl)$ | $(CH_3)_2CO$ | | $k$ AB | 45 | 4.7 | -6 | | | | | ([4]) |
| .32 | $C_6H_5CH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 1.01 | -3 | | | | * | ([1]) |
| .33 | $p\text{-}CH_3C_6H_4CH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 1.45 | -3 | | | | * | ([1]) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .34 | o-$CNC_6H_4CH_2Cl$ + $C_6H_5NH_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 2.20 | -5 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 3.75 | -5 | | | | | |
| | | | " " | | 45 | 9.00 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 1.16 | -4 | | | | | |
| .35 | o-$CNC_6H_4CH_2Cl$ + $C_6H_5NHC_2H_5$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 1.89 | -5 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 3.38 | -5 | | | | | |
| | | | " " | | 45 | 7.60 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 9.50 | -5 | | | | | |
| .36 | o-$CNC_6H_4CH_2Cl$ + $C_6H_5N(CH_3)_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 5.30 | -6 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 1.05 | -5 | | | | | |
| | | | " " | | 45 | 2.45 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 2.82 | -5 | | | | | |
| .37 | m-$CNC_6H_4CH_2Cl$ + $C_6H_5NH_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 2.02 | -5 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 3.30 | -5 | | | | | |
| | | | " " | | 45 | 8.00 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 1.11 | -4 | | | | | |
| .38 | m-$CNC_6H_4CH_2Cl$ + $C_6H_5NHC_2H_5$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 2.09 | -5 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 3.55 | -5 | | | | | |
| | | | " " | | 45 | 7.95 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 1.10 | -4 | | | | | |
| .39 | m-$CNC_6H_4CH_2Cl$ + $C_6H_5N(CH_3)_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 8.15 | -6 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 1.46 | -5 | | | | | |
| | | | " " | | 45 | 3.18 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 4.50 | -5 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .40 | $p$-$CNC_6H_4CH_2Cl + C_6H_5NH_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 1.67 | -5 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 2.78 | -5 | | | | | |
| | | | " " | | 45 | 6.80 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 8.80 | -5 | | | | | |
| .41 | $p$-$CNC_6H_4CH_2Cl + C_6H_5NHC_2H_5$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 1.63 | -5 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 3.02 | -5 | | | | | |
| | | | " " | | 45 | 6.85 | -5 | | | | | |
| | | | 0.2 0.05 | | 50 | 8.50 | -5 | | | | | |
| .42 | $p$-$CNC_6H_4CH_2Cl + C_6H_5N(CH_3)_2$ | $CH_3OH$ | A = 0.2; B = 0.05 | $k$ AB | 30 | 6.00 | -7 | | | | * | (3) |
| | | | 0.4 0.1 | | 35 | 1.25 | -6 | | | | | |
| | | | " " | | 45 | 2.90 | -6 | | | | | |
| | | | 0.2 0.05 | | 50 | 3.36 | -6 | | | | | |
| .43 | $m$-$NO_2C_6H_4CH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 5.06 | -4 | | | | * | (1) |
| .44 | $p$-$NO_2C_6H_4CH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 3.70 | -4 | | | | * | (1) |
| .45 | $m$-$NO_2C_6H_4CH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 7.30 | -4 | | | | * | (1) |
| .46 | $p$-$NO_2C_6H_4CH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 6.01 | -4 | | | | * | (1) |
| .47 | $p$-$ClC_6H_4CH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 7.33 | -4 | | | | * | (1) |
| .48 | $p$-$BrC_6H_4CH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 6.83 | -4 | | | | * | (1) |
| .49 | $p$-$IC_6H_4CH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 7.50 | -4 | | | | * | (1) |
| .50 | $C_6H_5COCH_2Cl + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 2.50 | -6 | | | | * | (1) |
| .51 | $C_6H_5COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 2.40 | -5 | | | | * | (1) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .52 | $C_6H_5COCH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 2.47 | -4 | | | | * | (1) |
| .53 | $C_6H_5COCH(CH_3)Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.16 | -5 | | | | * | (1) |
| .54 | $p$-$CH_3C_6H_4COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.90 | -4 | | | | * | (1) |
| .55 | $p$-$CH_3C_6H_4COCH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.83 | -4 | | | | * | (1) |
| .56 | $p$-$CH_3OC_6H_4COCH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.66 | -4 | | | | * | (1) |
| .57 | $m$-$NO_2C_6H_4COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 7.3 | -4 | | | | * | (1) |
| .58 | $p$-$NO_2C_6H_4COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 5.8 | -4 | | | | * | (1) |
| .59 | $m$-$NO_2C_6H_4COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 7.8 | -4 | | | | * | (1) |
| .60 | $p$-$NO_2C_6H_4COCH_2I + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 6.9 | -4 | | | | * | (1) |
| .61 | $m$-$NO_2C_6H_4COCH(CH_3)Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 4.3 | -5 | | | | * | (1) |
| .62 | $p$-$NO_2C_6H_4COCH(NO_2)\ Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 4.18 | -7 | | | | * | (1) |
| .63 | $p$-$ClC_6H_4COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 3.22 | -4 | | | | * | (1) |
| .64 | $p$-$BrC_6H_4COCH_2Br + C_6H_5NH_2$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 3.24 | -4 | | | | * | (1) |

## SOLVENTS

Et 90 = $H_2O$ + $C_2H_5OH$ 90 %

## COMMENTS

**General.** Data of ([1]): The first-order *k* is pseudomonomolecular, valid for the given concentrations, not independent of A/B. **(.5) (.6)** Slight autocatalytic effect. **(.19)** The reaction is formulated

$$2\ A + 2\ B \longrightarrow C_6H_5NHC_2H_5{\cdot}HCl + (C_6H_5CH_2)_2(C_6H_5)N{\cdot}HCl;$$

the rate measured is the formation of $Cl^-$. **(.20)** Formulated

$$2\ A + 2\ B \longrightarrow C_6H_5N(CH_3)_2{\cdot}HCl + (C_6H_5CH_2)_2(C_6H_5)N{\cdot}HCl;$$

rate measured is formation of $Cl^-$. **(.34)** Formulated

$$2\ A + 2\ B \longrightarrow C_6H_5NH_2{\cdot}HCl + (o\text{-}CNC_6H_4CH_2)_2(C_6H_5)N{\cdot}HCl.$$

**(.35) - (.41)** As (.34).

## LITERATURE

([1]) J. W. Baker, *CSL* **1932**, 1148, 2631; **1933**, 1128. ([1a]) D. P. Evans, H. B. Watson, R. Williams, *CSL* **1939**, 1345. ([2]) D. P. Evans, *CSL* **1944**, 422. ([2a]) K. J. Laidler, *CSL* **1938**, 1787. ([3]) D. H. Peacock, Potha, *CSL* **1937**, 955. ([4]) D. H. Peacock, *CSL* **1935**, 6.



942151 O—51——42

# ADDITION

## Aromatic halide + aromatic amine

## Quaternary base formation

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^{\circ} \times 10^{n}$ | | $E$ | $A = A^{\circ} \times 10^{n}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^{\circ}$ | $n$ | | $A^{\circ}$ | $n$ |
| .1 | $2,4\text{-}(NO_2)_2C_6H_3Br + C_6H_5NH_2$ | | B = 0.1; A = 0.4 - 0.8 | $k$ AB | 35 | 1.63 | -4 | | | |
| | | | " 0.4 | | 45 | 3.00 | -4 | 11.2 | 1 | 6 |
| .2 | $2,4\text{-}(NO_2)_2C_6H_3Br + m\text{-}CH_3C_6H_4NH_2$ | | B = 0.1; A = 0.4 | $k$ AB | 35 | 2.30 | -4 | | | |
| | | | | | 45 | 4.18 | -4 | 11.6 | | |
| .3 | $2,4\text{-}(NO_2)_2C_6H_3Br + p\text{-}CH_3C_6H_4NH_2$ | | B = 0.1; A = 0.4 | $k$ AB | 35 | 5.31 | -4 | | | |
| | | | | | 45 | 9.19 | -4 | 10.6 | 1 | 6 |

## LITERATURE

A. Singh, D. H. Peacock, *CSL* 1935, 1410.

# ADDITION

## Quaternary base formation

## Aromatic acyl halide + Aromatic amine

*Liquid phase*

Reaction type $ArCOCl + Ar'NH_2 \rightarrow (ArCO)Ar'NH_2^+ + Cl^-$

Rate measured $+ d[Cl^-]/dt$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_5COCl + C_6H_5NH_2$ | $C_6H_6$ | A = 0.005; B = 0.01 | $k$AB | 5.0 | 3.08 | -2 | |
| | | | | | 25.0 | 7.48 | -2 | |
| | | | | | 40.0 | 1.22 | -1 | |
| | | | | | 70.0 | 4.17 | -1 | 7.3 |
| .2 | $C_6H_5COCl + p\text{-}CH_3C_6H_4NH_2$ | $C_6H_6$ | A = 0.0025; B = 0.005 | $k$AB | 5.0 | 1.34 | -1 | |
| | | | | | 15.0 | 2.07 | -1 | |
| | | | | | 25.0 | 2.98 | -1 | |
| | | | | | 40.0 | 5.52 | -1 | 6.8 |
| .3 | $C_6H_5COCl + m\text{-}NO_2C_6H_4NH_2$ | $C_6H_6$ | A = 0.0025 - 0.01; B = 0.005 - 0.02 | $k$AB | 25.0 | 4.5 | -4 | 10.5 |
| .4 | $C_6H_5COCl + p\text{-}NO_2C_6H_4NH_2$ | $C_6H_6$ | A = 0.2; B = 0.01 | $k$AB | 25.0 | 4.2 | -5 | |
| | | | | | 40.0 | 1.1 | -4 | |
| | | | | | 70.0 | 6.2 | -4 | |
| | | | | | 100 | 2.5 | -3 | 11.8 |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|
| .5 | $C_6H_5COCl + p\text{-}ClC_6H_4NH_2$ | $C_6H_6$ | A = 0.005; B = 0.01 | $k$ AB | 5.0 | 6.8 | -3 | |
| | | | | | 25.0 | 1.63 | -2 | |
| | | | | | 40.0 | 2.98 | -2 | |
| | | | | | 70.0 | 9.5 | -2 | 7.6 |
| .6 | $p\text{-}CH_3C_6H_4COCl + C_6H_5NH_2$ | $C_6H_6$ | A = 0.0025; A = 0.005 | $k$ AB | 5.0 | 1.64 | -2 | |
| | | | | | 25.0 | 3.91 | -2 | |
| | | | | | 40.0 | 7.46 | -2 | |
| | | | | | 70.0 | 2.39 | -1 | 7.8 |
| .7 | $p\text{-}NO_2C_6H_4COCl + C_6H_5NH_2$ | $C_6H_6$ | A = 0.005; B = 0.0025 | $k$ AB | 5.0 | 2.86 | -1 | |
| | | | | | 15.0 | 3.65 | -1 | |
| | | | 0.01 0.005 | | 25.0 | 6.07 | -1 | |
| | | | 0.005 0.0025 | | " | 5.81 | -1 | |
| | | | 0.005 0.0025 | | 40 | 8.71 | -1 | 5.9 |
| .8 | $p\text{-}NO_2C_6H_4COCl + p\text{-}NO_2C_6H_4NH_2$ | $C_6H_6$ | A = 0.1; B = 0.005 | $k$ AB | 25.0 | 9.7 | -5 | |
| | | | | | 40.0 | 2.14 | -4 | |
| | | | | | 70.0 | 9.30 | -4 | |
| | | | | | 100 | 4.09 | -3 | 10.4 |
| .9 | $p\text{-}ClC_6H_4COCl + C_6H_5NH_2$ | $C_6H_6$ | A = 0.005; B = 0.0025 | $k$ AB | 25.0 | 1.05 | -1 | |
| | | | | | 40.0 | 1.78 | -1 | |
| | | | | | 70.0 | 5.46 | -1 | 7.0 |

## LITERATURE

E. G. Williams, C. N. Hinshelwood, *CSL* **1934**, 1079.

# ADDITION

*Liquid phase*

## Alkyl halide + heterocyclic amine → Quaternary base

Reaction type $RX + C_5H_5N \rightarrow C_5H_5NR^+ + X^-$

Rate measured $+ dX^-/dt$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $CH_3I + C_5H_5N$ | $C_6H_6$ | | $k$ AB | 40 | 3.6 | -5 | | | | | (7) (10) |
| | | | | | 60.0 | 1.46 | -4 | | | | | (7) |
| | | | | | 80.3 | 5.24 | -4 | | | | | (7) (10) |
| | | | | | 99.5 | 1.21 | -3 | 14.3 | 3.9 | 5 | | " " |
| | | | | | 117.2 | 3.28 | -3 | | | | | |
| | | $C_6H_5NO_2$ | | $k$ AB | 24.8 | 31.8 | -4 | | | | | (7) |
| | | | | | 39.9 | 9.82 | -4 | | | | | |
| | | | | | 60.0 | 3.49 | -3 | | | | | |
| | | | | | 80.3 | 1.18 | -2 | 13.6 | 3.2 | 6 | | |
| | | AnW 40 | | $k$ AB | 25.0 | 1.76 | -4 | | | | | (6) |
| | | | | | 39.9 | 6.20 | -4 | | | | | |
| | | | | | 60.1 | 2.78 | -3 | | | | | |
| | | | | | 80.4 | 9.08 | -3 | 14.7 | 2 | 7 | | |
| | | Et 55.7 | | $k$ AB | 25.0 | 5.3 | -5 | | | | | (6) |
| | | | | | 39.9 | 2.11 | -4 | | | | | |
| | | | | | 60.1 | 1.15 | -3 | | | | | |
| | | | | | 80.4 | 5.95 | -3 | 18.2 | 1.1 | 9 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $CH_3I + \alpha\text{-}CH_3C_5H_4N$ | $C_6H_6$ | | $k$AB | 80.5 | 1.21 | -4 | | | | | (10) |
| | | | | | 99.8 | 3.62 | -4 | | | | | |
| | | | | | 119.2 | 9.10 | -4 | | | | | |
| | | | | | 139.4 | 1.57 | -3 | 12.2 | | | | |
| | | $C_6H_5NO_2$ | | $k$AB | 15.0 | 7.05 | -5 | | | | | (7) |
| | | | | | 24.9 | 1.46 | -4 | | | | | |
| | | | | | 40.1 | 4.51 | -4 | | | | | |
| | | | | | 60.0 | 1.77 | -3 | 13.9 | 2.6 | 6 | | |
| .2.1 | $CH_3I + C_2H_5OOCC_5H_4N$ | $C_6H_5NO_2$ | | $k$AB | 24.9 | 4.85 | -5 | | | | | |
| | | | | | 40.0 | 1.63 | -4 | | | | | |
| | | | | | 60.0 | 6.23 | -4 | 14.6 | 2.7 | 6 | | |
| .3 | $C_2H_5Br + C_5H_5N$ | $C_6H_6$ | | $k$AB | 80.5 | 7.25 | -6 | | | | | (10) |
| | | | | | 99.8 | 2.49 | -5 | | | | | |
| | | | | | 118.5 | 6.85 | -5 | | | | | |
| | | | | | 139.4 | 2.10 | -4 | 16.2 | | | | |
| .4 | $C_2H_5I + C_5H_5N$ | $C_6H_6$ | 0.4 - 0.77 | $k$AB | 25 | 7.8 | -7 | | | | | (8) |
| | | | | | 80.5 | 4.17 | -5 | | | | | (10) |
| | | | | | 99.7 | 1.38 | -4 | | | | | |
| | | | | | 118.2 | 3.27 | -4 | | | | | |
| | | | | | 139.3 | 1.07 | -3 | 15.7 | | | | |
| | | $(CH_3)_2CO$ | 0.7 | $k$AB | 25 | 1.0 | -5 | | | | | (8) |
| | | $C_2H_5OH$ | " | | " | 1.07 | -6 | | | | | |
| | | $C_4H_9OH$ | " | | " | 8.6 | -7 | | | | | |
| | | $C_6H_5NO_2$ | 0.2 - 1.0 | | " | 1.95 | -5 | | | | | |
| | | $(CH_3)_2CHOH$ | 0.7 | | " | 8.3 | -7 | | | | | |
| | | $(CH_3)_3COH$ | " | | " | 7.2 | -7 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $C_2H_5I + C_5H_5N$ *(continued)* | $C_2H_5CH(CH_3)OH$ | 0.7 | | 25 | 7.8 | -7 | | | | | |
| | | $CH_3OH$ | " | | " | 1.94 | -6 | | | | | |
| | | $C_3H_7OH$ | " | | " | 8.6 | -7 | | | | | |
| .5 | $C_3H_7Br + C_5H_5N$ | $C_6H_6$ | | $k$AB | 80.6 | 2.82 | -6 | | | | | (10) |
| | | | | | 99.7 | 1.01 | -5 | | | | | |
| | | | | | 117.7 | 2.50 | -5 | | | | | |
| | | | | | 139.4 | 7.82 | -5 | 15.9 | | | | |
| .6 | $(CH_3)_2CHBr + C_5H_5N$ | $C_6H_6$ | | $k$AB | 99.7 | 1.04 | -5 | | | | | (7) |
| | | | | | 121.0 | 3.90 | -5 | | | | | |
| | | | | | 138.0 | 1.09 | -4 | | | | | |
| | | | | | 149.8 | 1.96 | -4 | 18.0 | 4.2 | 5 | | |
| | | $C_6H_5NO_2$ | | $k$AB | 60.0 | 2.64 | -5 | | | | | (7) |
| | | | | | 80.1 | 1.13 | -4 | | | | | |
| | | | | | 100.2 | 4.28 | -4 | | | | | |
| | | | | | 112.0 | 1.33 | -3 | 16.7 | 2.7 | 6 | | |
| .7 | $C_3H_7I + C_5H_5N$ | $C_6H_6$ | | $k$AB | 80.6 | 1.47 | -5 | | | | | (10) |
| | | | | | 99.7 | 4.84 | -5 | | | | | |
| | | | | | 117.7 | 1.23 | -4 | | | | | |
| | | | | | 139.4 | 3.96 | -4 | 16.1 | | | | |
| .8 | $(CH_3)_2CHI + C_5H_5N$ | $C_6H_6$ | | $k$AB | 80.6 | 2.68 | -6 | | | | | (10) |
| | | | | | 99.6 | 9.0 | -6 | | | | | (9) (10) |
| | | | | | 121 | 2.95 | -5 | | | | | (9) |
| | | | | | 138.9 | 8.10 | -5 | | | | | " |
| | | | | | 150.8 | 1.51 | -4 | 17.9 | 2.8 | 5 | | " |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $(CH_3)_2CHI + C_5H_5N$ *(continued)* | $C_6H_5NO_2$ 25 % + $C_6H_6$ 75 % | | $k$ AB | 60 | 2.83 | -6 | | | | | (9) |
| | | | | | 80.2 | 1.21 | -5 | | | | | |
| | | | | | 99.9 | 4.25 | -5 | | | | | |
| | | | | | 121.0 | 1.37 | -4 | 16.3 | 2.2 | 5 | | |
| | | $C_6H_5NO_2$ 50 % + $C_6H_6$ 50 % | | $k$ AB | 60.0 | 8.45 | -6 | | | | | (9) |
| | | | | | 80.2 | 3.44 | -5 | | | | | |
| | | | | | 100.2 | 1.15 | -4 | | | | | |
| | | | | | 121.0 | 4.14 | -4 | 17.3 | 1.9 | 6 | | |
| | | $C_6H_5NO_2$ 75 % + $C_6H_6$ 25 % | | $k$ AB | 60 | 1.2 | -5 | | | | | (9) |
| | | | | | 80.2 | 9.4 | -5 | | | | | |
| | | | | | 99.6 | 2.10 | -4 | | | | | |
| | | | | | 121.0 | 5.71 | -4 | 17.6 | 4.5 | 6 | | |
| | | $C_6H_5NO_2$ | | $k$ AB | 40 | 4.0 | -6 | | | | | (9) |
| | | | | | 60 | 2.21 | -5 | | | | | |
| | | | | | 80 | 9.12 | -5 | | | | | |
| | | | | | 99.3 | 3.10 | -4 | 16.7 | 2.0 | 6 | | |
| | **Aryl - substituted alkyl halide** | | | | | | | | | | | |
| .9 | $C_6H_5CH_2Cl + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 1.5 | -6 | | | | * | (1) |
| .10 | $C_6H_5CH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 7.3 | -5 | | | | * | (1) |
| | | " | A = B = 0.025 | $k$ AB | 20 | 1.29 | -4 | | | | | (2) |
| | | | | | 30 | 3.07 | -4 | 15.3 | 3.3 | 7 | | |
| | | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 0 | 2.48 | -5 | | | | | (2) (4) |
| | | | | | 20 | 1.22 | -4 | | | | | |
| | | | | | 30 | 8.43 | -4 | | | | | |
| | | | | | 40 | 4.82 | -4 | 12.4 | 2.4 | 5 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | | |
| .10 | $C_6H_5CH_2Br + C_5H_5N$ *(continued)* | $H_2O + (CH_3)_2CO$ 90 % | A = B = 0.025 | $k$AB | 20 | 2.34 | -4 | | | | | (2) |
| | | | | | 40 | 1.05 | -3 | 13.7 | 3.9 | 5 | | |
| .11 | $C_6H_5CH_2I + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 8.5 | -5 | | | | * | (1) |
| .12 | $C_6H_5CH_2Br + \alpha\text{-}CH_3C_5H_4N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.8 | -5 | | | | | (2) |
| | | | | | 30 | 3.6 | -5 | | | | | |
| | | | | | 40 | 7.0 | -5 | 12.4 | 2.3 | 5 | | |
| .13 | $m\text{-}CH_3C_6H_4CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.43 | -4 | | | | | (4) |
| | | | | | 30 | 5.15 | -4 | 11.7 | | | | |
| .14 | $p\text{-}CH_3C_6H_4CH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.58 | -4 | | | | * | (1) |
| | | " | A = B = 0.025 | $k$AB | 20 | 2.84 | -4 | | | | | (2) |
| | | | | | 30 | 7.0 | -4 | 16.0 | 2.4 | 8 | | |
| | | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 0 | 4.2 | -5 | | | | | (2) |
| | | | | | 20 | 2.02 | -4 | | | | | (4) (2) |
| | | | | | 30 | 3.90 | -4 | | | | | (2) |
| | | | | | 40 | 7.15 | -4 | 11.9 | 4.3 | 5 | | (2) |
| | | | | | " | 7.98 | -4 | 12.5 | | | | (3) |
| | | $H_2O + (CH_3)_2CO$ 90 % | A = B = 0.025 | $k$AB | 20 | 4.20 | -4 | | | | | (2) |
| | | | | | 40 | 1.87 | -3 | 13.7 | 6.6 | 5 | | |
| .15 | $p\text{-}CH_3C_6H_4CH_2Br + \alpha\text{-}CH_3C_5H_4N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 3.2 | -5 | | | | | (2) |
| | | | | | 30 | 6.4 | -5 | | | | | |
| | | | | | 40 | 1.24 | -4 | 12.2 | 4 | 4 | | |
| .16 | $p\text{-}C_2H_5C_6H_4CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.81 | -4 | | | | | (3) |
| | | | | | 30 | 3.51 | -4 | | | | | |
| | | | | | 40 | 6.73 | -4 | 12.3 | 2.2 | 5 | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .17 | 2, 4-$(CH_3)_2C_6H_3CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 6.28 | -4 | | | | | (3) |
| | | | | | 30 | 1.25 | -3 | | | | | |
| | | | | | 40 | 2.40 | -3 | 12.2 | 7.9 | 5 | | |
| .18 | $p$-$(CH_3)_2CHC_6H_4CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.63 | -4 | | | | | (3) |
| | | | | | 40 | 6.50 | -4 | 12.6 | 3.9 | 5 | | |
| .19 | $m$-$(CH_3)_3CC_6H_4CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.22 | -4 | | | | | (4) |
| | | | | | 40 | 4.82 | -4 | 12.5 | | | | |
| .20 | $p$-$(CH_3)_3CC_6H_4CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.65 | -4 | | | | | (3) (4) |
| | | | | | 30 | 3.35 | -4 | | | | | |
| | | | | | 40 | 6.46 | -4 | 12.5 | 3.3 | 5 | | |
| .21 | $p$-$CH_3OC_6H_4CH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | | 30.5 | ∞ | | | | | | (1) |
| .22 | $m$-$NO_2C_6H_4CH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 2.26 | -5 | | | | * | (1) |
| | | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 9.9 | -5 | | | | | (4) |
| | | | | | 40 | 3.5 | -4 | 11.5 | | | | |
| .23 | $p$-$NO_2C_6H_4CH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 2.6 | -5 | | | | * | (1) |
| | | " | A = B = 0.025 | $k$AB | 20 | 4.2 | -5 | | | | | (2) |
| | | | | | 30 | 1.02 | -4 | 15.8 | 2.5 | 8 | | |
| | | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 0 | 2.3 | -5 | | | | | (2) (4) |
| | | | | | 20 | 1.12 | -4 | | | | | |
| | | | | | 30 | 2.26 | -4 | | | | | |
| | | | | | 40 | 4.33 | -4 | 12.3 | 1.7 | 5 | | |
| | | $H_2O + (CH_3)_2CO$ 90 % | A = B = 0.025 | $k$AB | 20 | 1.58 | -4 | | | | | (2) |
| | | | | | 40 | 7.16 | -4 | 13.8 | 3.3 | 6 | | |

652.477

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .24 | $p$-$NO_2C_6H_4CH_2Br$ + $\alpha$-$CH_3C_5H_4N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.2 | −5 | | | | | (2) |
| | | | | | 30 | 2.5 | −5 | | | | | |
| | | | | | 40 | 4.7 | −5 | 12.1 | 1.3 | 4 | | |
| .25 | 2, 4-$(NO_2)_2C_6H_3CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 2.28 | −4 | | | | | (3) |
| | | | | | 30 | 4.70 | −4 | | | | | |
| | | | | | 40 | 8.96 | −4 | 12.4 | 4.0 | 5 | | |
| .26 | $m$-$FC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 9.5 | −5 | | | | | (4) |
| | | | | | 40 | 3.62 | −4 | 12.5 | | | | |
| .27 | $p$-$FC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.22 | −4 | | | | | (4) |
| | | | | | 40 | 5.78 | −4 | 12.5 | | | | |
| .28 | $m$-$ClC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.08 | −4 | | | | | (4) |
| | | | | | 40 | 4.07 | −4 | 12.1 | | | | |
| .29 | $p$-$ClC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.27 | −4 | | | | | (4) |
| | | | | | 40 | 5.10 | −4 | 12.7 | | | | |
| | | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 5.3 | −5 | | | | * | (1) |
| .30 | $m$-$BrC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.07 | −4 | | | | | (4) |
| | | | | | 40 | 3.77 | −4 | 11.5 | | | | |
| .31 | $p$-$BrC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.30 | −4 | | | | | (4) |
| | | | | | 40 | 5.19 | −4 | 12.6 | | | | |
| | | Et 90 | A = 0.025; B = 0.25 | $k$ A | 30.5 | 5.0 | −5 | | | | * | (1) |
| .32 | $m$-$IC_6H_4CH_2Br$ + $C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$ AB | 20 | 1.14 | −4 | | | | | (4) |
| | | | | | 40 | 4.13 | −4 | 11.8 | | | | |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .33 | $p$-$IC_6H_4CH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 1.48 | -4 | | | | | (4) |
| | | | | | 40 | 5.43 | -4 | 11.9 | | | | |
| | | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 5.5 | -5 | | | | * | (1) |
| | **Benzoyl - substituted alkyl halide** | | | | | | | | | | | |
| .34 | $C_6H_5COCH_2Cl + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.83 | -6 | | | | * | (1) |
| .35 | $C_6H_5COCH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.08 | -4 | | | | * | (1) |
| | | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 7.9 | -4 | | | | | (5) |
| | | | | | 40 | 2.83 | -3 | 11.7 | | | | |
| .36 | $C_6H_5COCH_2I + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 8.3 | -5 | | | | * | (1) |
| .37 | $o$-$CH_3C_6H_4COCH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 5.5 | -4 | | | | | (5) |
| .38 | $p$-$CH_3C_6H_4COCH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 7.4 | -4 | | | | | (5) |
| | | | | | 40 | 2.62 | -3 | 11.6 | | | | |
| | | EtOH | A = 0.025; B = 0.25 | $k$A | 30.5 | 9.2 | -5 | | | | * | (1) |
| .39 | 2, 4-$(CH_3)_2C_6H_3COCH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 5.0 | -4 | | | | | (5) |
| | | | | | 40 | 1.82 | -3 | 11.8 | | | | |
| .40 | $p$-$(CH_3)_3CC_6H_4COCH_2Br + C_5H_5N$ | $(CH_3)_2CO$ | A = B = 0.025 | $k$AB | 20 | 5.7 | -4 | | | | | (5) |
| | | | | | 40 | 2.0 | -3 | 11.5 | | | | |
| .41 | $m$-$NO_2C_6H_4COCH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.88 | -4 | | | | * | (1) |
| .42 | $p$-$NO_2C_6H_4COCH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.73 | -4 | | | | * | (1) |

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .43 | $p$-$ClC_6H_4COCH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.20 | -4 | | | | * | (1) |
| .44 | $p$-$BrC_6H_4COCH_2Br + C_5H_5N$ | Et 90 | A = 0.025; B = 0.25 | $k$A | 30.5 | 1.20 | -4 | | | | * | (1) |

## SOLVENTS

An W 40 = $H_2O$ 40 g + $(CH_3)_2CO$ 100 ml

Et 55.7 = $H_2O + C_2H_5OH$ 55.7 vol %

Et 90 = $H_2O + C_2H_5OH$ 90 vol %

## COMMENTS

Data of (1) : the pseudomonomolecular $k$ is not independent of A/B.

## LITERATURE

(1) J. W. Baker, *CSL* **1933**, 1128; **1932**, 2631. (2) J.W. Baker, W. S. Nathan, *CSL* **1935**, 519. (3) J.W.Baker, W.S. Nathan, *CSL* **1935**, 1840. (4) J.W.Baker, *CSL* **1936**, 1449. (5) J. W. Baker, *CSL* **1938**, 445. (6) R.A. Fairclough, C. N. Hinshelwood, *CSL* **1937**, 538. (7) K. J. Laidler, C. N. Hinshelwood, *CSL* **1938**, 858. (7a) K. J. Laidler, *CSL* **1938**, 1787. (8) J.F. Norris, S. W. Prentiss, *ACS* 1928, **50**, 3042. (9) H. C. Raine, C. N. Hinshelwood, *CSL* **1939**, 1378. (10) C.A. Winkler, C. N. Hinshelwood, *CSL* **1935**, 1147.

# ADDITION

## $SO_3$ to aromatic hydrocarbons

## Sulfonic acid formation

*Liquid phase*

Reaction type $ArH + SO_3 \longrightarrow ArSO_3H$

(A) (B) (L)

Rate measured $-dB/dt$

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $C_6H_6 + SO_3$ | $C_6H_5NO_2$ | A = 0.05 | $kAB^2$ | 3.1 | 1.72 | +1 | | (1) |
| | | | | | 40.1 | 4.88 | +1 | 4.8 | |
| .2 | $C_6H_5NO_2 + SO_3$ | $C_6H_5NO_2$ | A = 10.85<br>B = 0.3 - 1.0 | $kAB^2$ | 25 | 2.77 | -6 | | (1)(2) |
| | | | | | 40.0 | 7.85 | -6 | | |
| | | | | | 60.0 | 2.49 | -5 | | |
| | | | | | 80.0 | 4.98 | -5 | | |
| | | | | | 100.4 | 1.52 | -4 | 11.4 | |
| .3 | $p - CH_3C_6H_4NO_2 + SO_3$ | $C_6H_5NO_2$ | A = 1.5<br>B = 0.1 - 0.6 | $kAB^2$ | 0.0 | 6.14 | -5 | | (1)(3) |
| | | | | | 14.9 | 2.12 | -4 | | |
| | | | | | 24.9 | 4.16 | -4 | | |
| | | | | | 39.9 | 9.53 | -4 | | |
| | | | | | 60.0 | 2.36 | -3 | 11.0 | |





842510-51 — 43

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .4 | $p$ - $CH_3OC_6H_4NO_2 + SO_3$ | $C_6H_5NO_2$ | A = 0.10 | $kAB^2$ | 2.0 | 2.41 | 0 | | (1) |
| | | | | | 40.1 | 6.29 | 0 | 4.3 | |
| .5 | $C_6H_5Cl + SO_3$ | $C_6H_5NO_2$ | A = 0.4 | $kAB^2$ | 0.0 | 4.04 | -1 | | (1)(3) |
| | | | | | 14.9 | 8.63 | -1 | | |
| | | | | | 24.9 | 1.47 | 0 | | |
| | | | | | 39.9 | 2.40 | 0 | 7.7 | |
| .6 | $m$ - $C_6H_4Cl_2 + SO_3$ | $C_6H_5NO_2$ | A = 0.5 | $kAB^2$ | 1.9 | 5.50 | -3 | | (1) |
| | | | | | 40.1 | 4.36 | -2 | 9.2 | |
| .7 | $C_6H_5Br + SO_3$ | $C_6H_5NO_2$ | A = 0.25 | $kAB^2$ | 3.1 | 3.88 | -1 | | (1) |
| | | | | | 40.1 | 2.12 | 0 | 7.8 | |
| .8 | $\alpha$ - $C_{10}H_7NO_2 + SO_3$ | $C_6H_5NO_2$ | A = 0.25 | $kAB^2$ | 3.3 | 5.88 | -1 | | (1) |
| | | | | | 25.1 | 1.30 | 0 | 7.9 | |
| | | | | | 40.1 | 3.27 | 0 | | |

## COMMENTS

The rate laws are primarily given in the form $k'B^2$, and some data only in the from $kAB^2$. In the table, all data have been made uniform by dividing the original $k'$ by [A] (occasionally inferred from the conversion of $k'$ to $k$), and tabulation of values of $k$.

## LITERATURE

(1) E. Dresel, C. N. Hinshelwood, *CSL* **1944**, 649.

(2) D. R. Vicary, C. N. Hinshelwood, *CSL* **1939**, 1374.

(3) K. D. Wadsworth, C. N. Hinshelwood. *CSL* **1944**, 469.

# ASSOCIATION

## Unsaturated compounds → Alicyclic ring

*Gas phase*

Mass action is in M/l.

Rate measured $-\Delta p$

Rates are in M/l per sec.

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | |
| .1 | $CH_2{:}CHCH{:}CH_2 + CH_2{:}CHCHO \rightarrow C_7H_{10}O$ tetrahydrobenzaldehyde | A = 43 - 365 mm; B = 99 - 473 mm | $k$ AB | 155 | 1.37 | -4 | | | | * |
| | | | | 208 | 1.58 | -3 | | | | |
| | | | | 245 | 6.9 | -3 | | | | |
| | | | | 291 | 3.4 | -2 | | | | |
| | | | | 296 | 4.0 | -2 | | | | |
| | | | | 328 | 9.1 | -2 | | | | |
| | | | | 331 | 9.5 | -2 | 19.7 | 1.46 | 6 | |
| .2 | $CH_2{:}CHCH{:}CH_2 + CH_3CH{:}CHCHO \rightarrow C_8H_{12}O$ methyl-6-$\Delta^3$-tetrahydrobenzaldehyde | A = 92 - 224 mm; B = 393 - 440 mm | $k$ AB | 242 | 3.8 | -4 | | | | * |
| | | | | 250 | 5.5 | -4 | | | | |
| | | | | 277 | 1.55 | -3 | | | | |
| | | | | 296 | 3.1 | -3 | 22.0 | 9.0 | 5 | |
| .3 | *cyclo*-$C_5H_6 + CH_2{:}CHO \rightarrow C_8H_{10}O$ endomethylene-2, 5-tetrahydrobenzaldehyde | A = 45 - 363 mm; B = 42 - 328 mm; L = 15 - 64 mm | $k$ AB | 78 | 9.9 | -4 | | | | * |
| | | | | 93 | 1.4 | -3 | | | | |
| | | | | 108 | 3.1 | -3 | | | | |
| | | | | 120 | 5.4 | -3 | | | | |
| | | | | 144 | 1.55 | -2 | | | | |
| | | | | 167 | 3.9 | -2 | | | | |
| | | | | 184 | 7.25 | -2 | | | | |
| | | | | 205 | 1.54 | -1 | | | | |
| | | | | 210 | 2.03 | -1 | 15.2 | 1.5 | 6 | |

| No. | Reaction | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | | $E$ | $A = A^o \times 10^n$ | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $k^o$ | $n$ | | $A^o$ | $n$ | |
| .4 | $CH_2{:}CHC(CH_3){:}CH_2 + CH_2CHO \rightarrow C_8H_{12}O$ methyl-3-$\Delta^3$-tetrahydrobenzaldehyde | A = 39 - 340 mm; B = 50 - 432 mm | $k$ AB | 219 | 5.7 | -3 | | | | * |
| | | | | 247 | 1.55 | -2 | | | | |
| | | | | 292 | 6.6 | -2 | | | | |
| | | | | 299 | 8.2 | -2 | | | | |
| | | | | 332 | 2.0 | -1 | 18.7 | 1.02 | 6 | |
| .5 | $2\ CH_2{:}CHCH{:}CH_2 \rightarrow C_8H_{12}$ (dimer) | | $k\ A^2$ | 282 | 2.56 | -3 | | | | * |
| | | | | 291 | 3.37 | -3 | | | | |
| .6 | $2\ CH_2{:}CHC(CH_3){:}CH_2 \rightarrow C_{10}H_{16}$ (dimer) | | $k\ A^2$ | 245 | 6.5 | -4 | | | | * |

## COMMENTS

(.1) (.2) (.3) (.4) Association through Diels-Alder reaction. A small correction, averaging 3 %, was applied to allow for polymerization of A. Packing seems to have no effect. Reaction begins to reverse itself at higher temperatures. Data converted from $(M/ml)^{-1}\ sec^{-1}$ to $(M/l)^{-1}\ sec^{-1}$ units.

(.3) Initial $k$. Reverse reaction, see 581.441. (.5) $k$ at about 6 % reaction. (.6) The exptl. values are about 3/2 of those calculated from the collision theory.

## LITERATURE

G. B. Kistiakowsky, J. R. Lacher, *JACS* 1936, 58, 123.

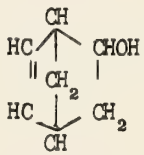
# ASSOCIATION

## Unsaturated compound + Alicyclic ring

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|
| .1 | $CH_2{:}CHCHO + CH{:}CHCH{:}CHCH_2 \rightarrow$  | $C_6H_6$ | $k$ AB | 40 | 3.3 | -4 | 13.7 |

## COMMENTS

Colorimetric determination.

## LITERATURE

A. Wassermann, *CSL* 1936, 1028.

# OXIDATION-REDUCTION

## Dismutation

### VI th group elements

*Liquid phase*

Amounts are in M/l.

Rates in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ S_2O_4^{--} + H_2O \rightarrow 2\ HSO_3^- + S_2O_3^{--}$ | $H_2O$ | $A \sim 0.3$; $L = 1.47$ | | | $k\,A^2$ | 0 | 4.0 | −6 | | | | * | (2) |
| | | | | | | | 10 | 6.5 | −6 | | | | | |
| | | | | | | | 20 | 1.05 | −5 | | | | | |
| | | | | | | | 30 | 1.8 | −5 | | | | | |
| | | | $A \sim 0.3$; $L = 0.98$ | | | " | 18 | 2.0 | −6 | | | | | |
| | | | 1.47 | | | | " | 8.8 | −6 | | | | | |
| | | | 2.64 | | | | " | 1.8 | −5 | | | | | |
| | | | 3.24 | | | | " | 3.1 | −5 | | | | | |
| .2 | $S_2O_6^{--} + H_2O \rightarrow SO_3^{--} + SO_4^{--}$ | $H_2O$ | 0.05 − 1.0 | | | $k\,A$ | 140 | 7 | −8 | | | | | |
| | | " | " | $H^+$ | 1.3 | $k\,A[H^+]$ | 50 | 1.2 | −6 | | | | * | (4) |
| | | | | | 0.4 | | 80 | 4.6 | −5 | | | | | |
| | | | | | 0.8 | | 85 | 1.1 | −4 | 29.8 | 1.6 | 14 | | |
| | | " | " | $OH^-$ | 0.20 | $k\,A[OH^-]$ | 119 | 1.9 | −5 | | | | | " |
| | | | | | 0.16 | | 140 | 1.0 | −4 | | | | | |
| | | | | | " | | 160 | 4.0 | −4 | | | | | |
| | | | | | " | | 180 | 1.45 | −3 | 25 | 1.6 | 8 | | |
| .3 | $UO_2^+ \rightarrow U^{VI} + U^{IV}$ | $H_2O$ | $A = 10^{-5} - 10^{-3}$ | $HClO_4$ | | $k\,A^2(H^+)$ | 25 | 1.3 | 2 | | | | * | (3) |
| | | | $\mu = 0.4$; $(H^+) = 0.02 - 0.3$ | | | | | | | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $UO_2^+ \rightarrow U^{VI} + U^{IV}$ *(continued)* | $H_2O$ | | $HClO_4 + NaClO_4$ (0.1) | | | | | | | | | | (3) |
| | | | $\mu = 0.119$; | | $(H^+) = 0.02 - 0.16$ | $k A^2(H^+)$ | 25 | 7.8 | 1 | | | | | |
| | | | 0.156 | | | | " | 8.0 | 1 | | | | | |
| | | | 0.192 | | | | " | 9.7 | 1 | | | | | |
| | | | 0.4 | | | | " | 1.3 | 2 | | | | | |

## COMMENTS

(.1) Recalculated from min., g/100 ml. The rate is approximately proportional to $[HSO_3^-]^2$. This is accounted for by (1) through evidence of two isomeric dithionous acids, reacting to form the observed products $HOSOSOOH + (HO)_2SSO_2 \rightleftarrows H_2S_2O_3 + H_2S_2O_5$; both isomers are stabilized by $HSO_3^-$, according to $HOSOSOOH + H_2O \rightleftarrows S(OH)_2 + H_2SO_3$; $S(OH)_2 + SO_2 \rightleftarrows (HO)_2SSO_2$. (.2) Evidence of partial reaction $S_2O_6^{--} \rightarrow 2\ SO_3^-$. The rate is not affected by $SO_3^{--}$, $SO_4^{--}$, $CrO_4^{--}$, or $BrO_3^-$, in neutral, acid, or alkaline solution. (.3) Polarography. $(H^+)$ is the activity of $H^+$ (quinhydrone electrode). Proposed mechanism $UO_2^+ + H^+ \rightarrow UOOH^{++}$; $UO^+ + UOOH^{++} \rightarrow UO_2^{++} + UOOH^+$ $(k')$; $UOOH^+ \rightarrow U^{IV}$ (stable); $k = k'/K$, where $K$ = dissociation constant of $UOOH^+$. From the fact that the $U^V/U^{VI}$ potential is independent of $(H^+)$ even in 0.5 $M$ $HClO_4$, $k'$ must be > 1300.

## LITERATURE

(1) H. Bassett, R. G. Durrant, *CSL* 1927, 1401.

(2) K. Jellinek, E. Jellinek, *ZPC* 1919, 93, 325.

(3) D. M. H. Kern, E. F. Orlemann, *JACS* 1949, 71, 2102.

(4) P. Goldfiner, H. D. Graf von Schweinitz, *ZPC* 1933, 22, 117.

# OXIDATION - REDUCTION

*Liquid phase*

## Dismutation

### VII th group element

Amounts are in M/l.

Rates are in M/l.per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $3\ Cl_2 + 3\ H_2O \rightarrow 6\ H^+ + 5\ Cl^- + ClO_3^-$ | $H_2O$ | | | | $+ dN/dt = kA^3/L^4M^3$ | 25 | 2 | -29 | | | | * | (40) |
| .2 | $Cl_2 + OH^- \rightarrow HOCl + Cl_3^-$ | $H_2O$ | | | | $kAB$ | 1.2 | ~ 8 | +12 | | $\Delta S_a =$ | | * | (28) |
| | | | | | | | 17.0 | " | " | 0 | 12.4 | | | |
| .3 | $ClO^- + 2\ HClO \rightarrow 2\ H^+ + 2\ Cl^- + ClO_3^-$ | $H_2O$ | A = 0.005; B = 0.005 | | | $kA$ | 25 | 6.5 | -7 | | | | *(a) | (45) |
| | | | 0.01 0.005 | | | | " | 7.1 | -7 | | | | | |
| | | | 0.01 0.01 | | | | " | 2.8 | -6 | | | | | |
| | | | 0.01 0.02 | | | | " | 1.0 | -5 | | | | | |
| | | " | 0.01 0.01 | $NaNO_3$ | 0.2 | " | " | 3.0 | -6 | | | | | " |
| | | | " " | NaCl | 0.2 | | " | 4.6 | -6 | | | | | |
| | | " | A = 1; B = 0.02 - 0.08 | | | $kAB^2$ | 15 | 1.9 | -2 | | | | *(b) | (10) |
| | | | | | | | 25 | 2.7 | -2 | | | | | |
| | | " | buffered solution | | | $-d(A + B)/dt = k'K[H^+]/([H^+] + K)$ | | | | | | | | |
| | | | | | | $= k(A + B)^3$ | | $k$ (max) | | | | | | |
| | | | B = 2A; $10^7[H^+] = 0.8 - 2.0$ | | | | 25 | 3.8 | -3 | | | | *(c) | (40,41) |
| | | " | $[H^+] \ll 3.6 \times 10^{-8}$ | | | $-dB/dt = k[H^+]^2A^3/K$ | | | | | | | | |
| | | | B ≪ A | | | | 25 | 2.6 | -2 | | | | *(d) | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $ClO^- + 2\ HClO \rightarrow 2\ H^+ + 2\ Cl^- + ClO_3^-$ | $H_2O$ | $[H^+] \gg 3.6 \times 10^{-8}$, $B \gg A$ | | | $-dA/dt = k\,K\,A^3/[H^+]$ | 25 | 2.7 | -2 | | | | *(e) | (40,41) |
| | *(continued)* | " | | | | $-dB/dt = B^3[H^+][Cl^-]/(k_1[H^+][Cl^-] + k_2B)$ | 25 | | | | | | *(f) | " |
| | | | | | | | $k_1$ | 4.6 | -4 | | | | | |
| | | | | | | | $k_2$ | 1.75 | -8 | | | | | |
| | | " | $[H^+]^2[Cl^-] \gg k_2B$ | | | $-dB/dt = kB^3/[H^+]$ | 25 | 9.7 | -10 | | | | *(g) | " |
| | | " | $k_2B \gg k_1[H^+]^2[Cl^-]$ | | | $-dB/dt = kB^2[H^+][Cl^-]$ | 25 | 5.7 | -11 | | | | *(h) | " |
| .4 | $3\ ClO^- \rightarrow ClO_3^- + 2\ Cl^-$ | $H_2O$ | | $OH^-$ | 0.1 | $kA^2$ | 25 | 2.5 | -8 | | | | * | (11,49,18,26) |
| | | | | | 0.5 | | " | 2.7 | -8 | | | | | |
| | | | | | 2.0 | | " | (3.3) | -7 | | | | | |
| | | | | | 0.1 | | 50 | 5.3 | -7 | | | | * | " |
| | | | | | 0.5 | | " | 5.8 | -7 | | | | | |
| | | | | | 2.0 | | " | (9.2) | -7 | | | | | |
| | | | | | 0.1 | | 90 | (5.5) | -5 | 25 | 1 | 12 | * | " |
| | | " | | $ClO_2^-$ | | $k_1A^2 + k_2A[ClO_2^-]$ | 25 | | | | | | * | " |
| | | | | | | | $k_1$ | 2.8 | -8 | | | | | |
| | | | | | | | $k_2$ | 9.7 | -7 | | | | | |
| | | | | | | | 50 | | | | | | | |
| | | | | | | | $k_1$ | 5.3 | -7 | | | | | |
| | | | | | | | $k_2$ | 1.4 | -6 | | | | | |
| .4.1 | $2\ ClO^- \rightarrow 2\ Cl^- + O_2$ | $H_2O$ | $A = 2.3$ | $OH^-$ | 0.1 | $+d(1/2O_2)/dt = kA^2$ | 30 | 6.7 | -8 | | | | * | (16) |
| | | | $A = 1$ | $NaCl = 2;\ \mu \sim 3$ | | | 45 | 3.8 | -7 | | | | | (48) |
| .5 | $6\ ClO + 3\ H_2O \rightarrow 5\ ClO_3^- + Cl^- + 6\ H^+$ | $H_2O$ | | HCl | 0.006 - 0.0115 | $kA^2[Cl^-] + k'A^2[Cl^-][H^+]$ | | | | | | | * | (4,5) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5.1 | $2\ ClO_2 + Cl^- + H_2O \longrightarrow HClO_2 + ClO_2^- + HClO$ | $H_2O$ | $[H^+] = 0.006 - 0.0115$ | | | $kA^2[Cl^-]$ | 60 | 9.3 | -4 | | | | * | (4,5) |
| .6 | $2\ ClO_2 + 2\ OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$ | $H_2O$ | | | | $kA^2B$ | 0<br>19 | 5<br>1.6 | 0<br>+1 | | | | * | (4) |
| .7 | $BrO^- + 2\ HBrO \longrightarrow 2\ H^+ + 2\ Br^- + BrO_3^-$<br>$(3\ HBrO + OH^- \longrightarrow 2\ H^+ + 2\ Br^- + BrO_3^- + H_2O)$<br>$(3\ Br_3^- + 6\ OH^- \longrightarrow 8\ Br^- + BrO_3^- + 3\ H_2O)$<br>(in not strongly alkaline solution) | $H_2O$ | | $-d([Br_2] + [HBrO])/dt =$ | | $k_a[Br_3^-]^3[OH^-]^4/[Br^-]^6$ | 25 | 4.0 | 21 | | | | $*_a$ | * |
| | | | | | | $k_b[HBrO]^3[OH^-]$ | 25 | 1.3 | 8 | | | | $*_b$ | * |
| | | | | | | $k_c[HBrO]^2[BrO^-]$ | 25 | 6.7 | 4 | | | | $*_c$ | * |
| | | | | | | $k_d[OH^-][Br_3^-]^2/[Br^-]^3$ | 25 | 1.1 | 3 | | | | $*_d$ | * |
| .7.1 | $(BrO^- + 2\ HBrO \longrightarrow 2\ H^+ + 2\ Br^- + BrO_3^-)$ | $H_2O$ | | | | $kAB^2$ | 0<br>25 | (1.2)<br>(1.7) | (-1)<br>(0) | | | | * | (19,26) |
| .7.2 | $3\ BrO^- \longrightarrow BrO_3^- + 2\ Br^-$<br>(in strongly alkaline solution) | $H_2O$ | | $OH^-$ | 1.89 | $kA^2$ | 80 | 9.3 | -4 | 25 | 1.7 | 12 | * | (19,26) |
| .7.3 | $2\ BrO^- \longrightarrow BrO_2^- + Br^-$ | $H_2O$ | | OH | 1.89 | $kA^2$ | 80 | 9.3 | -4 | 25 | 1.7 | 12 | * | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $3\ I_2 + 6\ OH^-$ | $H_2O$ | $[OH^-] > [I^-]$ | | | $k[OH^-][I_3^-]^2/[I^-]^3$ | 25 | 3.3 | -2 | | | | *a | (31) (32) |
| | $\rightarrow IO_3^- + 5\ I^- + 3\ H_2O$ | | $[OH^-] < [I^-]$ | | | $k[OH^-]^4[I_2]^3/[I^-]^6$ | 25 | 1.7 | 17 | | | | *b | (44) |
| | $(3\ I_3^- + 6\ OH^-$ | | $[OH^-] \ll [I^-]$ | | | $k[OH^-]^4[I_3^-]^3/[I^-]^6$ | 25 | 3.3 | 9 | | | | *c | (31) (32) |
| | $\rightarrow IO_3^- + 8\ I^- + 3\ H_2O)$ | | | | | | | | | | | | | |
| .9 | $I_2 + H_2O \rightarrow HIO + I^- + H^+$ | $H_2O$ | | | | $kA$ | 25 | (~ 4) | (-3) | | | | * | (1) |
| .10 | $3\ HIO + 3\ OH^-$ | $H_2O$ | $[OH^-] > [I_2]$ | | | $kA^2[I^-]/[OH^-]$ | 25 | 4.8 | -1 | | | | * | * |
| | $\rightarrow IO_3^- + 2\ I^- + 3\ H_2O$ | | | | | | 35 | 1.0 | 0 | | | | | |
| .11 | $3\ IO^- \rightarrow IO_3^- + 2\ I^-$ | $H_2O$ | strongly alkaline, low $[I^-]$ | | | $kA^2/[OH^-]$ | 25 | 3.3 | -2 | | | | | (32) (44a) |
| | | | | | | | 35 | 8.4 | -2 | | | | | (40) |
| | | | " " , high $[I^-]$ | | | $kA^2[I^-]/[OH^-]$ | 25 | 1.45 | 0 | | | | | " |
| | | | | | | | 35 | 3.0 | 0 | | | | | |

## COMMENTS

(.1) Calculation. The reaction is characteristic of solutions of high HCl concentration, where $ClO^-$ is negligible and HClO very small. $k = k'KK_h^3/3$; $k' = 0.027$ = third-order rate constant for $2\ HClO + ClO^- \rightarrow ClO_3^- + 2\ H^+ + 2\ Cl^-$; $K = [H^+][ClO^-]/[HClO] = 3.6 \times 10^{-8}$; $K_h = 1.01 \times 10^{-14}/3.6 \times 10^{-8}$. (.2) Calculated from data of Shilov and Solodushenkov, *C.R.Acad. Sci. USSR* 1936, 3, No. 1, p. 17. (.3) *(a)* $k$ over the first 50 % of the reaction; increases by about 25 % over the second half of the reaction. *(b)* Valid at low $[H^+]$ and very low $[Cl^-]$: HClO regenerated as fast as expanded. $k$ increases slightly with increasing $\mu$. (49) writes $-dA/dt = k'f^2AB^2$, with $\log f = 0.0289\ \mu$. *(c)* Low $[Cl^-]$. $K$ = ionization constant of HClO = $3.6 \times 10^{-8}$; $k$ is a function of $[H^+]$ and goes

## COMMENTS *(continued)*

through a maximum at the stated concentrations. *(d)* Low $[Cl^-]$. Low $[H^+]$. All hypochlorite practically A. $K = 3.6 \times 10^{-8}$; $k/K = 2 \times 10^{13}$. *(e)* Low $[Cl^-]$. High $[H^+]$. All hypochlorite practically B. $K = 3.6 \times 10^{-8}$; $kK = 9.7 \times 10^{-10}$. *(f)* Sufficiently high $[Cl^-]$; general rate law. *(g)* Special case of *(f)*; this case goes over into *(b)* by substituting $1/[H^+] = A/KB$, where $K = 3.6 \times 10^{-8}$. *(h)* Special case of *(f)*; cannot be realized experimentally, since even in solutions poor in $[H^+]$, $k_1[H^+]^2[Cl^-]$ is not negligible compared with $k_2B$; the value of $k$ is extrapolated. Mechanisms: ([11,12]) ([49]) $2\,H^+ + 2\,A \rightleftarrows 2\,B \rightleftarrows Cl_2O + H_2O$ (very fast); $(Cl_2 + H_2O) + A \rightarrow 2\,H^+ + 2\,Cl^- + ClO_3^-$ ( rate determining ). Mechanism of ([33]):
$2\,Cl_2 + H_2O \rightleftarrows HCl_3O + H^+ + Cl$ ; $HCl_2O + H_2O \rightleftarrows 2\,H^+ + 2\,Cl^- + HClO_2$; $HClO + HClO_2 \rightleftarrows H_2Cl_2O_3$; $Cl_2 + HClO_2 \rightleftarrows H^+ + Cl_3O_2^-$; $Cl_3O_2^- \rightleftarrows Cl_2O_2 + Cl^-$ ( rate determining ); $Cl_2O_2 + H_2O \rightleftarrows H_2Cl_2O_3$; $H_2Cl_2O_3 \rightleftarrows 2\,H^+ + Cl^- + ClO_3^-$. Pertinent literature: ([7]) ([9]) ([10]) ([11]) ([13]) ([15]) ([27]) ([33]) ([38]) ([39]) ([40]) ([43]) ([45]) ([49]) ([50])

**(.4)** The side reaction (.4.1) $2\,ClO^- \rightarrow Cl^- + O_2$ is generally negligible except at $OH^- > 0.5$ to above 50°C; data of $k$ in parentheses refer to experiments where evolution of $O_2$ was not negligible. In $OH^- = 2.0$, $k$ approached first order *(?)*. Mechanism of the reaction in alkaline solution:
$2\,ClO^- \rightarrow ClO_2^- + Cl^-$ (rate determining);
$ClO^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$ (faster). ([18]) writes for the rate determining step $HClO + ClO^- \rightarrow ClO_2^- + H^+ + Cl^-$, so that $-d[ClO^-]/dt = (k'/[OH^-])[ClO^-]^2$. **(.4.1)** For the total reaction $-dA/dt = k_F K A^3/[OH^-]^2 + kA^2$, where $k_F$ = Foerster's ([10]) rate constant (see reaction .3, *b*). The tabulated second-order $k$ for evolution of $O_2$ is constant up to 50 %. In $OH^- = 0.94$, the entire reaction is second-order. In terms of $\mu$, in solutions A = 1.0, linearity between log $k$ and $\sqrt{\mu}$ holds up to $\mu = 4$; with further increasing $\mu$, the observed $k$ falls short of the predicted. **(.5) (.5.1)** In sealed tube. $ClO_3^-$ and $Cl^-$ produced in the ratio 5:1. Reaction ( 4.1) is the primary step of (.4); ten-degree temperature coefficient ~ 2.2 (0° - 60°C); $k'$ is not evaluated. With increasing $[H^+]$, the rate increases somewhat, but not in proportion to $[H^+]$. If $ClO_2$ is continuously blown out with air, the reaction
$3\,ClO_2^- + 2\,HClO \rightarrow ClO_3^- + 2\,Cl^- + 2\,ClO_2 + H_2O$ was found to occur ([11]). **(.6)** Initial $k$, increasing with time. With excess $OH^-$, the rate becomes second-order in $ClO_2$. Addition of $Cl^-$ or $Cl_2$, or of $Cl^- + ClO_3^-$, has little effect on $k$. Assumed rate determining step $2\,ClO_2 + OH^- \rightarrow ClO_3^- + HClO_2$, followed by $HClO_2 + OH^- \rightarrow ClO_2^- + H_2O$, fast. **(.7)** Reaction in not very strongly alkaline solution. Rate laws *a*, *b*, *c*, are interconvertible with the aid of the

## COMMENTS *(continued)*

equilibrium constants, $[Br_3^-][OH^-]/[HBrO][Br^-] = 3.2 \times 10^{-5}$; $[H^+][BrO^-]/[HBrO] = 2 \times 10^{-11}$; $K = [Br_2][Br^-]/[Br_3^-] = 0.067$; $K_h = [HBrO][Br^-][H^+]/[Br_2] = 5.8 \times 10^{-9}$; $[HBrO][Br^-]^2/[Br_3^-][OH^-] = (3.1 \times 10^4)^3$; $[HBrO][OH^-]/[BrO^-] = 0.5 \times 10^{-3}$. Rate law *d* was considered ([47]) to represent a "rapid" reaction $2\ HBrO \rightarrow BrO_3^- + 2\ Br_2 + H^+ + 2\ H_2O$, other than the "slow" reaction (.7); however, according to ([26]), solutions of HBrO are more stable than implied by this reaction, and the data of ([47]) can be equally well interpreted by rate law *d*, analogous to F. Foerster's law of $ClO_3^-$ formation (see .3, *b*). Literature ([14])([19])([31,32])([46,47])([29])([24])([25])([26])([41])([45])([30])([7]). **(.7.1)** Older data of ([19]), recalculated by ([26]), and showing, for a rate law entirely identical with, (.7, *c*), a very considerable divergence of the numerical values of *k*; illustrating the wide spread of the experimental data; probably superseded by the value of ([26]) under (.7, *c*). **(.7.2)(.7.3)** In strongly alkaline solution; calculated by ([26]) from data of ([19]). Reaction (.7.3) taken to be the rate determining step of (.7.2). **(.8)** Slightly alkaline solutions, iodine in excess (colored solutions). Direct reaction, not through $IO^-$. Rate law *(b)* can be derived from $d[IO_3^-]/dt = [HIO_3]^3/[H^+]$ by successively substituting $HI_3O = K[I_2]/[H^+][I^-]$ and $[H^+] = 10^{-14}/[OH^-]$. Rate law *(c)* is then obtained by substituting $[I_2] = K'[I_3^-]/[I^-]$. Mechanisms proposed ([31])([32])([6])([33])([34]): $2\ I_3^- + OH^- \rightleftarrows HI_3O + 3\ I^-$, fast (or $I_2 + HIO \rightleftarrows HI_3O$, fast); $HI_3O + H_2O \rightarrow 2\ H^+ + 2\ I^- + HIO_2$, rate determining; *or*, $3\ I_3^- + 4\ OH^- \rightleftarrows 6\ I^- + I_3O_2^- + 2\ H_2O$, fast; $I_3O_2^- \rightarrow I_2O_2 + I^-$, rate determining; $HI_3O$ and $I_3O_2^-$ are supposed to be in equilibrium throughout the process. **(.9)** From rate calculations involving $H_2O_2$, $I^-$, and $I_2$; according to ([22,23,24]) *k* is much greater than the value estimated by ([1]).

**(.10)** Colorless solution. Mechanism ([31,32])([6])([33,34]) $I_2 + OH^- \rightleftarrows HIO + I^-$ (fast, far to the right); $2\ HIO + I^- \rightleftarrows HI_3O + OH^-$, fast; $HI_3O + H_2O \rightarrow 2\ H^+ + 2\ I^- + HIO_2$, rate determining. Literature ([10a])([12a])([5])([32])([26a])([6])([33]).

**(.11)** Colorless solutions. Low $[I^-]$ obtained by solid AgI and $Ag_2O$. The two rate laws cannot be superposed ([44a]).

## LITERATURE

(1) E.Abel, *ZPC* 1928, **136**, 161. (2) E.Abel, F.Fabian, *MHC* 1938, **71**, 241. (3) J.Bhaduri, *ZAC* 1897, **13**, 385. (4) W.C.Bray, *ZAC* 1906, **48**, 217. (5) W.C.Bray, *ZPC* 1906, **54**, 463, 569. (6) W.C.Bray, *ACS* 1930, **52**, 3580. (7) R.M.Chapin, *ACS* 1934, **56**, 2211. (8) E.Chirnoaga, *CSL* 1928, **2**, 1693. (9) W.Ebert, J.Naussbaum, Monographien über angew. Elektrochem, #38. (10) F.Foerster, J. prakt. Chem. 1901, **63**, 141. (10a) F.Foerster, J. prakt. Chem. 1903, **7**, 640.

(11) F.Foerster, P.Dolch, *ZEC* 1917, **23**, 137. (12) F.Foerster, P.Dolch, *ZEC* 1917, **23**, 145. (12a) F.Foerster, K.Gyr, *ZEC* 1903, **9**, 1. (13) F.Foerster, F.Jorre, *JPC* 1899, **59**, 53. (14) F.Foerster, E.Müller, F.Jorre, J. prakt. Chem. 1899, **59**, 53; *ZEC* 1899, **6**, 11. (15) J.M.Gallart, Anales soc. espan. fis. quim. 1933, **31**, 422. (16) A.F.Giordani, *GCI* 1924, **54**, 844. (17) O.R.Howell, *PRS* 1923, **104A**, 134. (18) H.Kaufmann, *ZAC* 1924, **37**, 364. (19) H.Kretzschmar, *ZEC* 1904, **10**, 789. (20) E.Lennsen, J.Lowenthal, *JPC* 1862, **86**, 216.

(21) J.R.Lewis, *JPC* 1928, **32**, 243. (22) H.A.Liebhafsky, *JPC* 1931, **155**, 289. (23) H.A.Liebhafsky, *ZAC* 1932, **54**, 1792. (24) H.A.Liebhafsky, *ACS* 1932, **54**, 3499. (25) H.A.Liebhafsky, *ACS* 1939, **61**, 3513. (26) H.A.Liebhafsky, B.Makower, *JPC* 1933, **37**, 1037. (26a) O.Liévin, *Compt. rend.* 1922, **174**, 868. (27) E.Müller, O.Müller, Nernst Festschrift (Halle, 1912) p. 319. (28) J.C.Morris, *ACS* 1946, **68**, 1692. (29) F.Pollak, E.Doktor, *ZAC* 1931, **196**, 80. (30) C.F.Prutton, S.H.Maron, *ACS* 1935, **57**, 1652.

## LITERATURE *(continued)*

(31) A.Skrabal, *ZEC* 1911, **17**, 665. (32) A.Skrabal, *MHC* 1911, **32**, 815. (33) A.Skrabal, *ZEC* 1934, **40**, 232. (34) A.Skrabal, *MHC* 1934, **64**, 289. (34) A.Skrabal, *MHC* 1935, **65**, 275. (36) A.Skrabal, *MHC* 1935, **66**, 129. (37) A.Skrabal, *ZEC* 1936, **42**, 228. (38) A.Skrabal, *MHC* 1939, **72**, 200. (39) A.Skrabal, *MHC* 1940-41, **73**, 269. (40) A.Skrabal, *ZEC* 1942, **48**, 314

(41) A.Skrabal, *ZEC* 1942, **48**, 323. (42) A.Skrabal, *MHC* 1943, **74**, **293**. (43) A.Skrabal, Z.Berger, *MHC* 1937, **70**, 168. (44) A.Skrabal, J.Gruber, *MHC* 1916, **37**, 535. (44a) A.Skrabal, R.Hohlbaum, *MHC* 1916, **37**, 191. (45) A.Skrabal, R.Skrabal, *MHC* 1938, **71**, 251. (46) A.Skrabal, S.R.Weberitsch, *MHC* 1915, **36**, 211. (17) A.Skrabal, S.R.Weberitsch, *MHC* 1915, **36**, 237. (48) W.F.Underwood, E.Mack jr., *JPC* 1931, **35**, 2650. (49) J.J.Weiss, *ZAC* 1930, **192**, 97. (50) J.F.White, M.C.Taylor, G.P.Vincent, *IEC* 1942, **34**, 782.

# OXIDATION - REDUCTION

## of compounds of the same element

### V th group element

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|
| .1 | $NH_4^+ + NO_2^- \longrightarrow N_2 + H_2O$<br>$(NH_4NO_2 \longrightarrow N_2 + H_2O)$<br>$(NH_4^+ + HNO_2 + OH^- \longrightarrow N_2 + 2\,H_2O)$ | $H_2O$ | A = 0.05 - 1.0<br>B = 0.005 - 0.187 | $H^+$ = 0.2; $\mu$ = 0.5<br>0.6 1.6<br>0.6 2.5 | $k\,K\,AB^2/[H^+]$ | 25<br>"<br>" | 1.7<br>2.5<br>3.2 | -2<br>-2<br>-2 |

## COMMENTS

Maintained equilibria, $HNO_2 \rightleftharpoons HNO_3$, NO; $HNO_2 \rightleftharpoons H^+ + NO_2^-$ ( $K = 5.6 \times 10^{-4}$ ).

## LITERATURE

(1) E. Abel, H. Schmid, J. Schafranik, *ZPC* 1931, Bodenstein Festband, 510.

(2) H. Schmid, *Atti X° Congr. Intern. Chim.* 1938, 2, 484.



942151 O—51——44

# OXIDATION-REDUCTION
## of compounds of the same element



### VI th group element

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Ionic strength | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ S_2O_3^{--} + S_2O_8^{--} \rightarrow 2\ SO_4^{--} + S_4O_6^{--}$ | $H_2O$ | A = 0.02; B = 0.01 | | $\mu$ = 0.09 | $k$B | 25 | 3.2 | −6 | (1) |
| | | | | | 0.11 | | " | 4.7 | −6 | |
| | | | | | 0.15 | | " | 7.5 | −6 | |
| | | " | " | $10^5$ $[Cu^{++}]$ = 0.0125-2.5 | $\mu$ = 0.09 | $k$B $[Cu^{++}]$ | 25 | 7.6 | 0 | (2) |
| | | | | | 0.11 | | " | 8.8 | 0 | |
| | | | | | 0.15 | | " | 1.2 | +1 | |
| | | " | " | KI | $\mu$ = 0.11 | $k$B $[I^-]$ | 25 | 2.8 | −3 | (2) |

## COMMENTS

For the uncatalyzed reaction, $\Delta \log k / \Delta\sqrt{\mu} \sim 4$. Authors conclude that the salt effect indicates the rate determining step to be A + B ; the rate, however, is nearly independent of B. The kinetics of the $Cu^{++}$ - catalyzed reaction is consistent with the hypothesis that the rate determining step is between two negative ions, one of which is a complex cupro-thiosulfate ion. For the KI-catalyzed reaction, $2\ I^- + S_2O_8^{--} \rightarrow I_2 + 2\ SO_4^{--}$ .

## LITERATURE

(1) C.V. King, O.F. Steinbach, *ACS* 1930, **52**, 4779. (2) C. V. King, O.R. Steinbach, *ACS* 1930, **52**, 4785.

# OXIDATION - REDUCTION
## of compounds of the same elements

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

### VII$^{th}$ group

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $Cl^- + 6\ HClO \rightarrow 3\ Cl_2 + ClO_3^- + 3\ H_2O$ (Williamson's reaction) | $H_2O$ | See Comments | | | $k\ A^4B/L$ | 25 | 1.1 | -3 | | * | ([35]) |
| .1.1 | $Cl^- + HClO \rightarrow Cl_2 + OH^-$ | $H_2O$ | | | | $k\ AB$ | 1.2<br>17.6 | 6.7<br>1.4 | 1<br>2 | | * | ([29a])<br>([38a])<br>([25]) |
| .2 | $2\ Cl^- + 2\ ClO_3^- + 4\ H^+ \rightarrow 2\ ClO_2 + Cl_2 + 2\ H_2O$ | $H_2O$ | A = 0.02 - 0.04<br>B = 1.5 - 2.0<br>$H^+$ = 1.5 - 2.0 | | | $k\ A^2B^2[H^+]^4$ | 50 | 1.7 | -5 | | * | ([24]) ([37]) |
| | | $H_2O$ | | HI | | $k\ AB\ [H^+]^2$ | 30<br>38.6 | 3.0<br>6.0 | -6<br>-6 | | * | ([9]) ([12]) |
| .3 | $5\ Cl^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Cl_2 + 3\ H_2O$ | $H_2O$ | HCl = 0.5 - 1.0 | | | $k\ AB^2[H^+]^2$ | 70 | 2.5 | -5 | | * | ([26]) |
| .3.1 | $5\ Cl^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Cl_2 + 3\ H_2O$ | $H_2O$ | | $H_3AsO_3$ | | $k\ AB[H^+]^2$ | 25<br>55 | 7.5<br>4.2 | -7<br>-5 | | * | ([19]) ([37]) |
| .4 | $5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ | $H_2O$ | $10^3[H^+]$ = 9.2; $\sqrt{\mu}$ = 0.463<br>125 0.395<br>29 0.212<br>→ 0 | | | $k\ AB[H^+]^2$ | 25<br>"<br>"<br>" | 2.7<br>3.1<br>6.0<br>9.0 | 0<br>0<br>0<br>0 | | * | ([38]) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ | $H_2O$ | 216 | 0.506 | | $k\ AB[H^+]^2$ | 25 | 6.0 | 0 | | * | (14) |
| | *(continued)* | | 67 | 0.303 | | | " | 3.7 | 0 | | | |
| | | | | → 0 | | | " | 9.0 | 0 | 15.8 | | |
| | | | | | | | | | (25 – 65°; $\mu$ = 0.1) | | | |
| | | " | | $\sqrt{\mu}$ = 0.9 | | " | 25 | 2.4 | 0 | | * | (29) |
| | | | | 0.5 | | | " | 2.9 | 0 | | | |
| | | | | 0.2 | | | " | 4.6 | 0 | | | |
| | | | | → 0 | | | " | 9.5 | 0 | 13.6 | | |
| | | | | | | | | | (0 – 32°C; $\mu$ = 0.1) | | | |
| .5 | $I^- + HIO + H^+ \rightarrow I_2 + H_2O$ | $H_2O$ | | | | $k\ AB[H^+] - k'L$ | 25 | | | | * | (1) |
| | | | | | | | $k$ | 1.3 | 10 | | | |
| | | | | | | | $k'$ | ~ 4 | -3 | | | |
| .6 | $5\ I^- + IO_3^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$ | $H_2O$ | $A > 10^{-4}$ | | | $k\ A^2B[H^+]^2 f$ | 25 | 1.3 | 9 | | * | (8) |
| | | | | | | | 35 | 1.7 | 9 | | | |
| | | | | | | | 25 | 5.2 | 8 | | * | (3) |
| | | " | " | $I_2$ | sat | $k\ AB[I_3^-][H^+]^2 f^4$ | | | | | | (8) |
| | | | | | | | 25 | 9.2 | 8 | | * | |
| | | | | | | | 35 | 1.2 | 9 | | | |
| | | " | " | $I_2$ | sat | $AB[H^+]^2(k'A + k''[I_3^-])E$ | | | | | * | (6) |
| | | | | | | | 25 | | | | | |
| | | | | | | | $k'$ | 1.2 | 9 | | | |
| | | | | | | | $k''$ | 1.0 | 9 | | | |
| | | | | | | | 50 | | | | | |
| | | | | | | | $k'$ | 2.0 | 9 | | | |
| | | | | | | | $k''$ | 1.6 | 9 | | | |
| | | " | $A < 10^{-8}$ | | | $k\ AB[H^+]^2$ | 25 | 4 | 2 | | ** | " |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | E | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .6 | $5\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$ | $H_2O$ | $10^{-8} < A < 10^{-4}$ | | | $AB[H^+](kf^2 + k'AF' + k''[I_3^-]F')$ | | | | | *** | ([13]) |
| | *(continued)* | | | | | | 25 | | | | | |
| | | | | | | | $k$ | 4 | 2 | | | |
| | | | | | | | $k'$ | 1.3 | 8 | | | |
| | | | | | | | $k''$ | 9.1 | 8 | | | |
| | | $D_2O$ | $A < 10^{-8}$ | | | $k\,A^2B[H^+]^2f$ | 25 | 5.1 | 9 | | * | |
| .7 | $7\,I^- + IO_4^- + 8\,H^+ \rightarrow 4\,I_2 + 4\,H_2O$ | $H_2O$ | See reactions (.7.1) (.7.2) | | | | | | | | | |
| .7.1 | $2\,I^- + IO_4^- + 2\,H^+ \rightarrow I_2 + IO_3^- + H_2O$ | $H_2O$ | | $H_2SO_4$ | | $AB(k'F + k''F'[H^+]^2)$ | | | | | * | ([4]) ([7]) |
| | | | | | | | 25 | | | | | |
| | | | | | | | $k'$ | 2.2 | 1 | | | |
| | | | | | | | $k''$ | 2.3 | 5 | | | |
| .7.2 | $2\,I^- + IO_4^- + 2\,H^+ \rightarrow I_2 + IO_3^- + H_2O$ | | $CH_3COOH + CH_3COO^-$ buffer | | | $k\,AB$ | | | | | * | ([4]) |
| | | | | $CH_3COO^- = 0$ | | | 25 | 6.3 | 0 | | | |
| | | | | $CH_3COO^- = 0.1$ | | | " | 9.1 | 0 | | | |
| | | | $CH_3COOH = 0.1$, | $CH_3COO^- = 0.4$ | | | " | 1.2 | + | | | |

## COMMENTS

(.1) Williamson's reaction ([40, 17, 30, 34]) occurs when the alkaline reserve of an unbuffered NaClO solution has been depleted so that HClO, HCl, and $Cl_2$, are greatly in excess of over $ClO^-$. $k$ calculated from the reactions (1) $3\ HClO \rightarrow 3\ H^+ + 2\ Cl^- + ClO_3^-$, (2) $3\ Cl_2 + 3\ H_2O \rightarrow 6\ H^+ + 5\ Cl^- + ClO_3^-$, (3) $H^+ + Cl^- + HClO \rightleftarrows H_2O + Cl_2$, occurring with NaCl and enough $H_2SO_4$ added to NaClO to convert $ClO^-$ entirely to HClO; the amount of $Cl^-$ was such that after conversion of $ClO^-$ to $ClO_3^-$, $HClO/Cl^- = 6:1$. Williamson's reaction is composed of (1) and (3); $k = k_F K/K_H$, where $k_F$ = Foerster's rate constant for $ClO^- + 2\ HClO \rightarrow ClO_3^- + 2\ Cl^- + 2\ H^+ = 2.7 \times 10^{-2}$ (see 712.770), $K\ (HClO) = 3.6 \times 10^{-8}$, $K_H = 1.01 \times 10^{-14}/3.6 \times 10^{-8}$. Substantial evidence in support of the above calculation ([36]). (.1.1) Derived from the reverse reaction and equilibrium. (.2) $ClO_2$ and $Cl_2$ continuously blown out by a stream of air. The $k\ A^2B^2[H^+]$ - order reaction is more nearly $k\ A^{1.55}B^{1.9}[H^+]^{3.9}$. This approximately eighth order is considered real by F. Foerster, *ZEC* 1917, 23, 137; J. Hirade, *Bull. Chem. Soc. Japan* 1935, 10, 109, holds the findings to be vitiated by salt effects. Mechanisms proposed: ([12]) $Cl^- + ClO_3^- + 2\ H^+ \rightarrow HClO + HClO_2$, rate determining; $HClO_2 + HClO \rightarrow ClO_2 + 1/2\ Cl_2 + H_2O$, fast; ([24]) $2\ Cl^- + 2\ ClO_3^- + 4\ H^+ \rightleftarrows H_2ClO_3 + Cl_2$; $H_2ClO_3 \rightarrow ClO_2 + H_2O$; $4\ H^+ + 4\ Cl^- + H_2ClO_3 \rightarrow 5/2\ Cl_2 + 3\ H_2O$; ([37]) for the eighth-order reaction, $HCl + HClO_3 \rightleftarrows H_2Cl_2O_3$; $H_2Cl_2O_3 \rightleftarrows Cl_2O_2 + H_2O$; $2\ Cl_2O_2 \rightleftarrows Cl_4O_4$; $Cl_4O_4 \rightleftarrows Cl_2 + Cl_2O_4$; $Cl_2O_4 \rightleftarrows 2\ ClO_2$; ([37]) for the fourth-order reaction, $HCl + HClO_3 \rightleftarrows H_2Cl_2O_3$ (rapid); $H_2Cl_2O_3 \rightleftarrows HClO_2 + HClO$ (rate determining); $HCl + HClO \rightleftarrows H_2O + Cl_2$; $HClO_2 + HClO_3 \rightleftarrows H_2Cl_2O_5$; $H_2Cl_2O_5 \rightleftarrows H_2O + Cl_2O_4$; $Cl_2O_4 \rightleftarrows 2\ ClO_2$; the eighth order results when the products of $H_2Cl_2O_3 \rightarrow HClO_2 + HClO$ are not rapidly removed and the mobile equilibrium $H_2Cl_2O_3 \rightleftarrows Cl_2O_2 + H_2O$ can be established. (.3) Mechanism proposed $2\ Cl^- + ClO_3^- + 2\ H^+ \rightarrow ClO^- + 2\ HClO$; $ClO^- + 2\ Cl^- + 2\ H^+ \rightarrow Cl_2 + H_2O$; $HClO + H^+ + Cl^- \rightarrow Cl_2 + H_2O$. This mechanism is the reverse of the hypochlorite formation from $Cl_2$. However, ([12]) claims that recalculation of the data of ([26]) shows fourth order; ([24]) opposes the disregard of $ClO_2$ in the scheme of ([26]). Reaction between $NaClO_3$ and concentrated HCl in a sealed tube at 60°C gave ([11]) $ClO_2/Cl_2$ = 1/2000. The rate law $k\ AB[H^+]^2$, established by ([12]) for dilute HCl in the presence of $I^-$, is held by ([37]) to be valid in highly concentrated HCl which acts as depolarizer (.3.1) Derived from $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$, in the presence of HCl. In concentrated HCl, order higher than $[H^+]^2$. (.4) Data of ([38]): direct measurements; data of ([14]) derived from $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ catalyzed by $Br_2 + Br^-$; data of ([29]) with allyl alcohol used to remove HBrO. $k$ extrapolated to $\mu = 0$ in good agreement. Assumed mechanism, $Br^- + BrO_3^- + 2\ H^+ \rightarrow HBrO_2 + HBrO$ (or $H_2Br_2O_3$), rate determining, followed by rapid reactions of HBr with

## COMMENTS *(continued)*

HBrO and $HBrO_2$. A fifth-order reaction $5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ was expected by ([33]) at very high $Br^-$; ([15]) found no evidence therefor at $\mu < 0.7$ and HBr up to 0.1; however, with $Br^- = 4.2$ and $[H^+] = 0.009$, the fourth-order $k$ increased, indicating a possible higher-order reaction. (.5) Calculated ([1]) from data on rates involving $H_2O_2$, $I^-$, $I_2$, and the hydrolysis constant of $I_2 = 3 \times 10^{-13}$; $k'$ is for the reverse reaction $I_2 + H_2O$. However, ([21,22,23]) concludes that $k'$ must be considerably greater than $4 \times 10^{-3}$, hence $k$ considerably less than $1.3 \times 10^{10}$. (.6) *Notation:* $f$ = activity coefficient of univalent ion; $\log F = -4\ \mu\sqrt{j} + 0.90\ j$; $\log F' = -2.20\sqrt{j}$; $j = \Sigma\ c_i z_i^2$. Reactions without $I_2$: iodine shaken out with $CCl_4$ as soon as formed; otherwise saturated with $I_2$. ** Solutions in equilibrium with solid $AgIO_3$ and AgI; in the presence of $H_2SO_4$; effects of electrolytes negligible. *** includes the effects of electrolytes; when $I^-$ is very small, $I_3^-$ has no effect on the rate. Reaction in $D_2O$: measured in 91 % $D_2O$, extrapolated to 100 %. Mechanisms proposed: * for $I^- > 10^{-4}$: ([31, 13]) $I^- + IO_3^- + 2\ H^+ \rightleftarrows H_2I_2O_3 \rightleftarrows I_2O_3 + H_2O$, fast; $I_2O_3 + I^- \rightarrow I_3O_2^-$, rate determining; $I_2O_3^- + 6\ I^- + 4\ H^+ \rightarrow 3\ I_3^- + 2\ H_2O$ (succession of fast steps); similar more elaborate mechanisms, ([33]). ([2]) $2\ I^- + IO_3^- + 2\ H^+ \rightarrow IO^- + 2\ HIO$, slow; $I^- + I_3^- + IO_3^- + 2\ H^+ \rightarrow 2\ HIO + I_3O^-$, slow; $I^- + IO_3^- + 2\ H^+ \rightarrow HIO_2 + HIO$, slow; fast reactions $HI + HIO_2 \rightarrow 2\ HIO$; $HI + HIO \rightarrow I_2 + H_2O$. ** and ***, for $I^- < 10^{-4}$: ([5, 2]) $I^- + IO_3 + 2\ H^+ \rightarrow HIO_2 + HIO$, rate determining; fast reactions $HI + HIO \rightarrow I_2 + H_2O$; $3\ HI + HIO_2 \rightarrow 2\ I_2 + 2\ H_2O$. ([13, 20]) $I^- + IO_3^- + 2\ H^+ \rightarrow H_2I_2O_3$; $H_2I_2O_3 \rightarrow HIO_2 + HIO$, rate determining. The kinetic improbability of rapid reactions of high order was argued by ([39]). ([33]) defended rapid equilibria of high order, but regarded them as built up by a succession of reactions very fast in comparison with the rate determining step. (.7) (.7.1) Reaction (.7) is composed of (.7.1), followed by reaction (.6). In strongly acid solutions low in A and high in B, only reaction (.7.1) occurs. $\log F = 0.71\sqrt{j}$; $\log F' = -2.20\sqrt{j}$; $j = \Sigma\ c_i z_i^2$. (.7.2) In acetate buffer, mechanism proposed ([4]) $I^- + IO_4^- \rightarrow IO_3^- + IO^-$, rate determining; $I^- + IO^- + 2\ H^+ \rightarrow I_2 + H_2O$, fast.

## LITERATURE

(1) E. Abel, *ZPC* 1928, **136**, 161. (2) E. Abel, *ZPC*[A] 1931, **154**, 167. (3) E. Abel, F. Fabian, *MHC* 1938, **71**, 153. (4) E. Abel, A. Fürth, *ZPC* 1923, **107**, 313. (5) E. Abel, H. Hilferding, *ZPC* 1928, **136**, 186. (6) E. Abel, H. Hilferding, O. Smetana, *ZPC*[B] 1936, **32**, 91. (7) E. Abel, R. Siebenschein, *ZPC* 1927, **130**, 631. (8) E. Abel, F. Stadler, *ZPC* 1926, **122**, 49. (9) W. C. Bray, *JPC* 1903, **7**, 92. (10) W. C. Bray, 1906, **48**, 215.

(11) W. C. Bray, *ZAC* 1906, **48**, 217. (12) W. C. Bray, *ZAC* 1906, **48**, 244. (13) W. C. Bray, *ACS* 1930, **52**, 3580. (14) W. C. Bray, P. R. Davis, *ACS* 1930, **52**, 1427. (15) W. C. Bray, H. A. Liebhafsky, *ACS* 1935, **57** 51. (16) S. Dushman, *JPC* 1904, **8**, 453. (17) J. L. Gay-Lussac, *Lieb. Ann.* 1842, **43**, 178 (footnote). (18) W. Judson, J. W. Walker, *CSL* 1898, **73**, 410. (19) H. Kubina, *MHC* 1922, **43**, 439. (20) H. A. Liebhafsky, *ACS* 1931, **53**, 2074.

(21) H. A. Liebhafsky, *ZPC* 1931, **155**, 289. (22) H. A. Liebhafsky, *ACS* 1932, **54**, 1792. (23) H. A. Liebhafsky, *ACS* 1932, **54**, 3499. (24) R. Luther, F. M. MacDougall, *ZPC* 1908, **62**, 199. (25) J. C. Morris, *ACS* 1946, **68**, 1692. (26) J. Sand, *ZPC* 1904, **50**, 465. (27) G. Schacherl, *Lieb. Ann.* 1876, **182**, 193. (28) H. Schlundt, R. B. Warder *ACJ* 1895, **17**, 754; 1896, **18**, 23. (29) M. Sclar, L. C. Riesch, *ACS* 1936, **58**, 667. (29a) E. A. Shilov, S. N. Solodushenkov, *C. R. Acad. Sci. URSS* 1936, **3**, 7. (30) A. Skrabal, 1907, **28**, 319.

(31) A. Skrabal, *MHC* 1911, **32**, 815. (32) A. Skrabal, *ZEC* 1924, **30**, 109. (33) A. Skrabal, *ZEC* 1934, **40**, 232. (34) A. Skrabal, *ZEC* 1934, **40**, 233. (see pp. 239-40). (35) A. Skrabal, *MHC* 1941, **73**, 269. (36) A. Skrabal, *ZEC* 1942, **48**, 314. (37) A. Skrabal, H. Schreiner, *MHC* 1934, **65**, 213. (38) A. Skrabal, S. R. Weberitsch, *MHC* 1915, **36**, 211. (38a) S. N. Solodushenkov, E. A. Shilov, *ZhFKh* 1945, **19**, 405; *APU* 1945, **31**, 23. (39) A. Thiel, 1928, **34**, 113. (40) A. W. Williamson, *Lieb. Ann.* 1845, **54**, 141.

(41) H. A. Young, W. C. Bray, *ACS* 1932, **54**, 4284.

# OXIDATION-REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** $H_2O_2$

**Oxidant:** VII group element

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $H_2O_2 + Br_2 \rightarrow 2\,Br^- + 2\,H^+ + O_2$ | $H_2O$ | HBr = 0.01 - 0.38 | $k$ AB/LM | 0 | 1.0 | -5 | * | (3) (4) (5) |
| | | | | | 25 | 3.0 | -4 | | |
| | | | | | 35 | 7.1 | -4 | | |
| .2 | $H_2O_2 + I_2 \rightarrow 2\,H^+ + 2\,I^- + O_2$ | $H_2O$ | | $k_1$AB/L$^2$M + $k_2$AB/LM | 25 | | | * | (1) (6) (7) (8) (10) (11) |
| | | | | | $k_1$ | 2.0 | -14 | | |
| | | | | | $k_2$ | 1.1 | -11 | | |
| .2.1 | $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ | $H_2O$ | | $k_1'$AB | 25 | 3.3 | +9 | * | " |
| .2.2 | $H_2O_2 + HIO \rightarrow H_2O + H^+ + I^- + O_2$ | $H_2O$ | | $k_2'$AB | 25 | 3.7 | +1 | * | " |
| .2.3 | $H_2O_2 + H^+ + I^- \rightarrow H_2O + HIO$ | $H_2O$ | | $k$ ABC | 25 | 1.6 | -1 | * | (11) |
| .3 | $H_2O_2 + IO_4^- \rightarrow H_2O + IO_3^- + O_2$ | $H_2O$ | A = 0.01 - 0.02<br>$10^3$B = 0.25 = 2.0<br>$H_2SO_4$ = 0.005 | $k$ AB | 0 | ~ 4.5 | -1 | * | (2) |
| | | | $10^3$A = 0.1<br>B = $1 \times 10^{-5}$<br>$H_2SO_4$ = 0.0025 | $k$ B | 25 | ~ 2.5 | -7 | * | (2) |

## COMMENTS

(.1) Derived from the reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$, catalyzed by $Br_2 + Br^-$. Mass-action expressed in activities of $H^+$ and $Br^-$. Assumed mechanism $Br_2 + H_2O \rightarrow HBrO + H^+ + Br^-$, followed by the rate determining step $H_2O_2 + HBrO \rightarrow H^+ + Br^- + H_2O + O_2$. (.2) Derived from the reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$, catalyzed by $I_2 + I^-$. (.2.1) (.2.2) are component steps of reaction (.2); $k_1' = k_1/K_1$, where $K_1 = [HIO][H^+]^2/[I_2] = 6 \times 10^{-24}$; $k_2' = k_2/K_2$, where $K_2 = [IO^-][H^+]^2[I]/[I_2] = 3 \times 10^{-13}$. (.2.3) Derived from $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ catalyzed by $I_2 + I^-$, and from $H_2O_2 + 2\ H^+ + 3\ I^- \rightarrow 2\ H_2O + I_3^-$. (.3) Initial rates only; $k$ falls with progressing reaction. No satisfactory general equation evolved.

## LITERATURE

(1) E. Abel, *ZPC* 1928, 136, 161. (2) E. Abel, J. Ziffer, *MHC* 1949, 80, 585. (3) W. C. Bray, R. S. Livingston, *ACS* 1923, 45, 1251. (4) W. C. Bray, R. S. Livingston, *ACS* 1923, 45, 1265, 2052. (5) W. C. Bray, R. S. Livingston, *ACS* 1928, 50, 1654. (6) H. A. Liebhafsky, *ACS* 1932, 54, 1792. (7) H. A. Liebhafsky, *ACS* 1932, 54, 3499. (8) H. A. Liebhafsky, *ACS* 1932, 54, 3504. (9) H. A. Liebhafsky, *ACS* 1939, 61, 3513. (10) H. A. Liebhafsky, A. Mohammad, *ACS* 1933, 55, 3977.

(11) G. Maganini, GCI 1891, 21, 746. (12) B. Makower, H. A. Liebhafsky, *TFS* 1933, 29, 598.

# OXIDATION - REDUCTION
## by ions of different elements

*Liquid phase*

**Reductant: I st group element**

**Oxidant: VI th " "**

Rates in M/l per sec.

| No. | Reaction | Solvent | Defined rate law | Temperature | log $k$ |
|---|---|---|---|---|---|
| .1 | $Ag^{+} + S_2O_8^{--} \longrightarrow Ag^{+++} + 2\ SO_4^{--}$ | $H_2O$ | $k$AB | 25 | $-1.93 - 0.38\sqrt{\mu}$ |

## COMMENTS

The formula for log $k$ obtained by graphic treatment, is the mean from the five $Ag^{+}$ - catalyzed reactions between $S_2O_8^{--}$ and $Cr^{+++}$, $VO^{++}$, $Mn^{++}$, $N_2H_5^{++}$, $Ce^{+++}$, for which this step is considered to be rate determining. The wide scattering of the experimental points around the Brönsted slope, and the presence of higher oxide of Ag as a solid phase, suggest that this rate determining step may have been oversimplified. For possible complexities, see ([3]) (GSF).

## LITERATURE

([1]) Bekier, Kijowski, *Roczniki Chem.* 1934, **14**, 1004 ($Mn^{++}$). ([2]) A.O.Dekker, H.A.Levy, D.M.Yost, *ACS* 1937, **59**, 2129 ($Mn^{++}$, $N_2H_5^{+}$). ([3]) C.V.King, *ACS* 1928, **50**, 2098. ([4]) D.M.Yost, *ACS* 1926, **48**, 152 ($Cr^{+++}$). ([5]) D.M.Yost, W.H.Claussen, *ACS* 1931, **53**, 3349. ($VO^{++}$).



National Bureau of Standards - National Research Council

May, 1950

# OXIDATION-REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** IV th group element

**Oxidant:** VIII th " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $Sn^{++} + 2\ Fe^{+++} \rightarrow Sn^{++++} + 2\ Fe^{++}$ (perchlorates) | $H_2O$ | A = 0.002–0.005<br>B = 0.004–0.05 | $HClO_4$ | | $k\,AB/[H^+]^2$ | | | | * | (2) |
| | | | | $[H^+]$=0.10; | $\sqrt{\mu}$ = 0.64–0.43 | | 70 | 6.0 | −4 | | |
| | | | | 0.05 | 0.28 | | " | 8.3 | −4 | | |
| | | $H_2O$ | | | $\mu \rightarrow 0$ | " | 55 | 4.3 | −5 | | |
| | | | | | | | 70 | 1.1 | −3 | | |
| .1.1 | $Sn^{++} + 2\ Fe(OH)_2^+ \rightarrow Sn^{++++} + 2\ Fe(OH)_2$ | $H_2O$ | " | | $\mu \rightarrow 0$ | $k'AB$ | 55 | 3.35 | −2 | * | (2) |
| | | | | | | | 70 | 1.55 | −1 | | |

## COMMENTS

Reaction (.1) assumed to proceed over $Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^+ (K_1)$; $FeOH^{++} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+ (K_2)$; $Sn^{++} + 2\ Fe(OH)_2^+ \rightarrow Sn^{++++} + 2\ Fe(OH)_2 (k')$, i.e. (.1.1) is the rate determining step of (.1); $k = 2\ k'K_1K_2$; at 55° and 70°C, $K_1$ = 0.0106 and 0.025; $K_1K_2 = 6.5 \times 10^{-4}$ and $35.2 \times 10^{-4}$.

## LITERATURE

(1) W. C. Bray, A. V. Hershey, *ACS* 1934, **56**, 1899.
(2) M. H. Gorin, *ACS* 1936, **58**, 1787.
(3) R. A. Robertson, N. H. Law, *TFS* 1935, **31**, 899.
(4) J. Weiss, *CSL* 1944, 309.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** V th group element

**Oxidant:** $O_2$

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $4\ V^{+++} + O_2 + 2\ H_2O \rightarrow 4\ VO^{++} + 4\ H^+$ | $H_2O$ | A = 0.008 - 0.08<br>$HClO_4$ = 0.02 - 0.09<br>$O_2$ = 0.2 - 1 atm. | $Cu^{++}$ | $10^5[Cu^{++}]$ | $kA/[H^+]$ | | | | |
| | | | | | 1 | | 25 | 3.7 | -4 | |
| | | | | | 2 | | " | 4.5 | -4 | |
| | | | | | 3 | | " | 1.15 | -3 | |
| | | | | | 10 | | " | 1.8 | -3 | 17.2 |

## COMMENTS

The rate is independent of $[O_2]$ if $[Cu^{++}] \geqslant 10^{-5}$. With $Cu^{++} \sim 10^{-7}$, the rate law of the nearly uncatalyzed reaction approaches the order $k'\ AB/[H^+]$, with $k' = 8.3 \times 10^{-6}$ at 25°C.

## LITERATURE

(1) W.C.Bray, J.B.Ramsey, *ACS* 1933, 55, 2279. (2) J.B.Ramsey, E.L.Colichman, L.C.Pack, *ACS* 1946, 68, 1695. (3) J.B.Ramsey, R.Sugimoto, H.DeVorkin, *ACS* 1941, 63, 3480.



94251 O -51 - 45

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** V th group element

**Oxidant:** I st " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | $k^o$ | $n$ |
| .1 | $H_3PO_2 + 2\,Ag^+ + H_2O \longrightarrow H_3PO_3 + 2\,Ag + 2\,H^+$ | $H_2O$ | A = 0.055 - 0.13<br>B = 0.05 - 1<br>$H^+$ = 0.035 - 0.07 | $kA$ | 25 | 2.2 | -5 |
| .1.1 | $n - H_3PO_2 \longrightarrow a - H_3PO_2$ | $H_2O$ | as (.1) | $kA$ | 25 | 2.2 | -5 |
| .2 | $H_3PO_2 + 2\,Cu^{++} + H_2O \longrightarrow H_3PO_3 + 2\,Cu^+ + 2\,H^+$ | $H_2O$ | See reactions (.1.1) and (.2.1) | | | | |
| .2.1 | $n - H_3PO_2 \longrightarrow a - H_3PO_2$ | $H_2O$ | A = 0.01<br>$Cu^{++}$ = 0.25 - 0.5<br>$H^+$ = 0.06 | $kA$ | 25 | 1.8 | -5 |
| .2.2 | $a - H_3PO_2 + 2\,Cu^{++} + H_2O \longrightarrow H_3PO_3 + 2\,Cu^+ + 2\,H^+$ | $H_2O$ | A = 0.02 - 0.075<br>B = 0.0035 - 0.025<br>$H^+$ = 0.04 ; 0.28 | $kAB^2/[H^+]^2$ | 25 | ~ 5 | -6 |

## COMMENTS

**(.1) (.1.1)** Reaction (.1.1) is the rate determining step of (.1); *n* = normal, *a* = active. The following step, $a - H_3PO_2 + 2\ Ag^+ + 2\ H_2O \longrightarrow H_3PO_3 + 2\ Ag^+ + 2\ H^+$, is so rapid that the rate of the tautomeric change (.1.1) can be fully isolated. **(.2) (.2.1) (.2.2)** The rate of reaction (.2) is determined by the rate of (.2.1) at very high $[Cu^{++}]$, but by the rate of (.2.2) at $[Cu^{++}] \ll H_3PO_2$, when the rate-determining importance of $a - H_3PO_2 + 2\ Cu^{++} + H_2O \longrightarrow H_3PO_3 + 2\ Cu^+ + 2\ H^+$ becomes predominant over the rate of the tautomerization $n \longrightarrow a$. The value of *k* for (.2.1) agrees closely with *k* for oxidation of $H_3PO_2$ in the presence of excess $I_2$ and $HgCl_2$.

## LITERATURE

(1) A.D.Mitchell, *CSL* 1920, **117**, 1322.

(2) A.D.Mitchell, *CSL* 1921, **119**, 1266.

(3) A.D.Mitchell, *CSL* 1922, **121**, 1624.

(4) A.D.Mitchell, *CSL* 1923, **123**, 629.

# OXIDATION-REDUCTION
## of compounds of different elements

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

**Reductant:** $V^{th}$ **group element**

**Oxidant:** $II^{nd}$ **group element**

| No. | Reaction | Solvent | Amount of reactant | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $H_3PO_2 + 2\ Hg^{++} + H_2O \rightarrow H_3PO_3 + Hg_2^{++} + 2\ H^+$ | $H_2O$ | A = 0.01 - 0.10<br>B = 0.012 - 0.18 | | $k\ A$ | 15<br>25 | 7.0<br>2.2 | -6<br>-5 | * | (3) |
| .2 | $H_3PO_3 + 2\ Hg^{++} + H_2O \rightarrow H_3PO_4 + Hg_2^{++} + 2\ H^+$ | $H_2O$ | A = 0.9<br>B = 0.0045 - 0.16<br>$H^+$ = 0.12 - 0.44 | NaCl 0.0 - 0.45 | $k\ A[H^+]/(1 + k'[H^+]/B)$ | 25 | $k \sim 2$<br>$k' \sim 1$ | -5<br>-5 | * | (6) |

## COMMENTS

(.1) $k$ is weighted average from the complete rate expression $([H^+] + m\ A)(1 - a)\ kt = \ln (A_o/A) + \ln ([H^+]_o/[H^+])$, where $a$ = degree of dissociation of $H_3PO_2$ at half-time, $m \sim 1.6$. The tautomerization $n - H_3PO_2 \rightarrow a - H_3PO_2$ (normal → active) is rate determining at the higher concentrations; the subsequent step $a - H_3PO_2 + Hg^{++}$ is to a minor extent rate determining at lower concentrations. See further (2)(4)(5). (.2) $k$ corrected for half-time dissociation of $H_3PO_3$; $k$ and $k'$ correspond to the steps: $n - H_3PO_3 \rightarrow a - H_3PO_3$ ($k'$); $a - H_3PO_3 \rightarrow n - H_3PO_3$ ($k_2$); $a - H_3PO_3 + 2\ Hg^{++} + H_2O \rightarrow H_3PO_4 + Hg_2^{++} + 2\ H^+$ ($k_3$); $k = k_1$; $k' = k_2/k_3$. In an acetate buffer (pH ~ 6) the rates were 160 times as fast as at pH ~ 1. See further (1).

## LITERATURE

(1) R.D.Griffith, A.McKeown, *TFS* 1940, 36, 766. (2) A.D.Mitchell, *CSL* 1920, 117, 1322. (3) A.D.Mitchell, *CSL* 1921, 119, 1266. (4) A.D.Mitchell, *CSL* 1922, 121, 1624. (5) A.D.Mitchell, *CSL* 1923, 123, 629. (6) A.D.Mitchell, *CSL* 1924, 125, 1013.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** V th group element

**Oxidant:** " " " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|
| .1 | $3\ H_3AsO_3 + 2\ HNO_3 \rightarrow 3\ H_3AsO_4 + 2\ NO + H_2O$ | $H_2O$ | A = 0.01 - 0.125<br>B = 0.30 - 3.0<br>NO, $p$ = 0.98 atm | $k\ \alpha\ [H^+]^{2/3}[NO_3^-]^{2/3}\ (p_{NO})^{4/3}$<br>$\alpha = [f^2/(46 + 22\ \mu)]^{2/3}$ | 25 | $k$ = 1.3 | -4 |

## COMMENTS

This rate law applies only to a system in which the quasi-stationery equilibrium $HNO_3 + 2\ NO + H_2O \rightleftarrows 3\ HNO_2$ is maintained at constant $p_{NO}$ which is usually 0.98 atm; $f$ = activity coefficient of $HNO_3$. Assumed rate determining step, $H_3AsO_3 + N_2O_3 \rightarrow H_3AsO_4 + 2\ NO + H_2O$.

## LITERATURE

E. Abel, H. Schmid, J. Weiss, *ZPC* 1930, **147**, 69.

# OXIDATION-REDUCTION

## of compounds of different elements

Reductant: V th group element

Oxidant: VI th " "

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NH_4 + 4\ S_2O_8^{--} + 3\ H_2O \rightarrow NO_3^- + 8\ SO_4^{--} + 10\ H^+$ | $H_2O$ | (A + B) = 0.002 | $Ag^+$ | $k\,B[Ag^+]$ | 25 | 2.7 | -2 | * | (2) |
| | | | 0.5 | | | " | 4.5 | -3 | | |
| | | | 1.0 | | | " | 3.7 | -3 | | |
| .2 | $3\ H_3PO_2 + H_2Cr_2O_7 + 6\ H^+ \rightarrow 3\ H_3PO_3 + 2\ Cr^{+++} + 4\ H_2O$ | $H_2O$ | A = 0.05 - 0.2; B = 0.001 - 0.15; $H^+$ = 0.07 - 4 | | $k\,AB$ | 25 | 8.0 | -6 | * | (3) |
| | | | | | | | - 1.4 | -5 | | |

## COMMENTS

(.1) Rate determining step, $S_2O_8^{--} + Ag^+ \rightarrow 2\ SO_4^{--} + Ag^{+++}$, followed by $n\ Ag^{+++} + NH_4^+ \rightarrow NO_3^-, H^+$. See further (1).

(.2) Mechanism assumes equilibrium between $n - H_3PO_2$ (normal) and $\alpha - H_3PO_2$ (active); the acid-catalyzed reaction $n - H_3PO_2 \rightarrow \alpha - H_3PO_2$ ($k_1$) and the reverse reaction ($k_2$) is rapid, and the rate determining step is $\alpha - H_3PO_2 + Cr_2O_7^{--} \rightarrow H_3PO_3 + Cr_2O_6^{--}$ ($k_2$), followed by the rapid reaction $2\ H_3PO_2 + Cr_2O_6^{--} + 8\ H^+ \rightarrow 2\ H_3PO_3 + 2\ Cr^{+++} + 4\ H_2O$; $k \sim 3\ k_1 k_3 / k_2$.

## LITERATURE

(1) C. V. King, *ACS* 1928, 50, 2080. (2) Marshall, Inglis, *PRS Edinburgh* 1900, 23, 163. (3) A. D. Mitchell, *CSL* 1924, 125, 564.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

Reductant: $V^{th}$ group element

Oxidant: $VII^{th}$ group element

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NO_2^- + I_2 + H_2O \rightarrow NO_3^- + 2\ I^- + 2\ H^+$ | $H_2O$ | buffers; pH = 6 (low $[I^-]$, or pH = 7 (high $[I^-]$; | | $k\ AB/(K + M)[(aM/A) + 1]$ | | | | | | | | * | ([3]) |
| | | | | | | | 40 | | | | | | | |
| | | | | | $\mu = 2.7$ | | $k$ | 4.9 | −7 | | | | | |
| | | | | | | | 50 | | | | | | | |
| | | | | | 0.7 | | $k$ | 4.7 | −6 | | | | | |
| | | | | | | | $a$ | 1.53 | +2 | | | | | |
| | | | | | 2.7 | | $k$ | 2.3 | −6 | | | | | |
| | | | | | | | $a$ | 1.61 | +2 | | | | | |
| | | | | | | | 60 | | | | | | | |
| | | | | | 0.7 | | $k$ | 1.9 | −5 | | | | | |
| | | | | | | | $a$ | 1.46 | +2 | | | | | |
| | | | | | 2.7 | | $k$ | 9.4 | −6 | | | | | |
| | | | | | | | $a$ | 1.40 | +2 | | | | | |
| .2 | $2\ N_3^- + I_2 \rightarrow 2\ N_2 + 2\ I^-$ | $H_2O$ | A = 0.005; B = 0.0001 | $NaClO_4$ | 0.01 | $k\ A[CS_2]$ | | | | | | | * | ([8]) |
| | | | | KI | 0.004 | | | | | | | | | |
| | | | | $CS_2$ | 0.009 | | 0.4 | 6.25 | −3 | | | | | |
| | | | | | 0.008 | | 10 | 2.34 | −2 | | | | | |
| | | | | | 0.007 | | 12.5 | 3.03 | −2 | | | | | |
| | | | | | 0.0004 | | 15 | 3.9 | −2 | | | | | |
| | | | | | 0.0002 | | 20 | 7.5 | −2 | 20 | 5.7 | 13 | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of Addend | Defined mass-action law | Temperature | $k = k^\circ \times 10^n$ $k^\circ$ | $n$ | $E$ | $A = A^\circ \times 10^n$ $A^\circ$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .3 | $3\ H_3PO_2 + IO_3^- \rightarrow 3\ H_2PO_3 + I^-$ | $H_2O$ | A = 0.05 - 0.01 | $H^+$ | 0.017 - | $k\,A[H^+]/(1 + k'[H^+]/B)$ | | | | | | | * | (7) |
| | | | B = 0.01 - 0.14 | | 0.037 | | 20.3 | | | | | | | |
| | | | | | | | $k$ | 1.0 | -3 | | | | | |
| | | | | | | | $k'$ | 3.5 | -1 | | | | | |
| | | | | | | | 30.1 | | | | | | | |
| | | | | | | | $k$ | 2.7 | -3 | 17 | | | | |
| | | | | | | | $k'$ | 4.4 | -1 | 4.5 | | | | |
| .4 | $H_3PO_2 + I_2 + H_2O \rightarrow H_3PO_3 + 2\ I^- + 2\ H^+$ | $H_2O$ | | | See Comments | | | | | | | | * | (6) |
| | | | pH > 6 | $2\ k_1B[H_2PO_3^-]K/(K + [I^-])$ | | | | | | | | | * | (6) |
| .4.1 | $H_2PO_2^- + I_2 + H_2O \rightarrow H_2PO_2^- + 2\ I^- + 2\ H^+$ | $H_2O$ | pH > 6 | | $\mu$ = 2.05 | $k_1AB$ | 30 | 2.7 | -4 | | | | | |
| | | | | | " | | 50 | 4.7 | -3 | | | | | |
| | | | | | " | | 60 | 1.5 | -2 | 25.2 | | | | |
| | | | | | 1.1 | | " | 1.2 | -2 | | | | | |
| .4.2 | $H_3PO_2 + I_2 + H_2O \rightarrow H_3PO_3 + 2\ I^- + 2\ H^+$ | $H_2O$ | $[I^-]$ = 0.002 - 0.2 | | $\mu$ = 0.25 | $k_2AB$ | 30 | 1.3 | 0 | 18 | | | * | (6) |
| .4.3 | $H_3PO_2 + I_3^- + H_2O \rightarrow H_3PO_3 + 3\ I^- + 2\ H^+$ | $H_2O$ | " | | " | $k_3AB$ | 30 | 3.8 | -1 | 18 | | | * | (6) |
| .5 | $H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2\ I^- + 2\ H^+$ | $H_2O$ | $HCO_3^-/CO_3^{--}$ | | $\mu$ = | $k\,AB$ | | | | | | | * | (5) |
| | | | 0.014/0.118 | | 0.60 | | 0.1 | 2.2 | -2 | | | | | |
| | | | " " | | " | | 10.0 | 1.2 | -1 | | | | | |
| | | | 0.10/0.10 | | " | | 20.0 | 5.6 | -1 | | | | | |
| | | | 0.014/0.118 | | 0.80 | | " | 2.8 | -1 | 22 | | | | |
| | | | $HPO_4^{--}/H_2PO_4^-$ | | | | | | | | | | | |
| | | | 0.013/0.120 | | 0.60 | | 0.1 | 2.1 | -2 | | | | * | " |
| | | | 0.30/0.10 | | 0.80 | | 10.0 | 4.5 | -2 | | | | | |
| | | | 0.014/0.12 | | 0.60 | | " | 1.15 | -1 | | | | | |
| | | | 0.10/0.033 | | 0.40 | | 20.0 | 2.40 | -1 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5.1 | $n - H_3PO_3 + H^+ \rightarrow H_3PO_3.H^+$ | $H_2O$ | pH < 1 | HX = | $\mu$ = | $k_1A[HX]$ | | | | | | | * | (5) |
| | | | | $H_3O^+$ | 0.5 - 0.6 | | 45 | 1.65 | -4 | | | | | |
| | | | | $H_3PO_3$ | " | | " | 1.05 | -4 | | | | | |
| | | | | $H_3PO_4$ | " | | " | 1.2 | -4 | | | | | |
| | | | | $HSO_4^-$ | " | | " | 9.35 | -5 | | | | | |
| | | | | $CH_3COOH$ | " | | " | 5,2 | -6 | | | | | |
| | | | | $CH_2ClCOOH$ | " | | " | 1.6 | -5 | | | | | |
| | | | | $CH_2OHCOOH$ | " | | " | 1.0 | -5 | 22.5 | | | | |
| .5.2 | $HPO_3^{--} + I_2 + H_2O \rightarrow HPO_4^{--} + 2\ I^- + 2\ H^+$ | $H_2O$ | 2 < pH < 9 | $\mu$ = 0.4 - 1.15 | | $k_2AB$ | 20 | 9.5 | +1 | | | | * | (5) |
| | | | | | 0.4 | | 30 | 3.3 | +2 | 22.0 | | | | |
| | | | | | 0.56 | | 45 | 1.6 | +3 | | | | | |
| .5.3 | $H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2\ I^- + 2\ H^+$ | $H_2O$ | | | | $k_3AB$ | 45 | 1.35 | -2 | | | | * | (5) |
| .5.4 | $H_3PO_3 + I_3^- + H_2O \rightarrow H_3PO_4 + 3\ I^- + 2\ H^+$ | $H_2O$ | | | | $k_4AB$ | 35 | 1.1 | -3 | | | | | |
| | | | | | | | 45 | 3.5 | -3 | 21.4 | | | | |
| .6 | $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$ | $H_2O$ | | HCl | $k\ B[H^+]^2[Cl^-]$ | | 25 | 7.5 | -7 | | | | * | (9) |
| | | | | | | | 55 | 3.8 | -5 | | | | | (20) |
| | | | | HBr | $k\ B[H^+]^2[Br^-] + k'L$ | | | | | | | | * | " |
| | | | | | | | 25 | | | | | | | |
| | | | | | | | $k$ | 1.55 | -6 | | | | | |
| | | | | | | | $k'$ | 5.15 | -7 | | | | | |
| | | | | HI | $k\ B[H^+]^2[I^-] + k'L$ | | | | | | | | * | " |
| | | | | | | | 25 | | | | | | | |
| | | | | | | | $k$ | 3.3 | -5 | | | | | |
| | | | | | | | $k'$ | 3.5 | -6 | | | | | |
| .7 | $3\ H_3AsO_3 + BrO_3^- \rightarrow 3\ H_3AsO_4 + Br^-$ | $H_2O$ | | HCl + $HClO_4$ | $k\ B[H^+][Cl^-]$ | | 25 | 1.5 | -3 | | | | * | (20) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .8 | $H_3AsO_3 + I_3^- + H_2O \rightarrow H_3AsO_4 + 2\,I^- + 2\,H^+$ | $H_2O$ | A = 0.022 - 0.044 | $HClO_4$ | | $k\,AB/[H^+][I^-]^2$ | 0 | 1.1 | -5 | | | | * | (10) (12) |
| | | | B = 0.005 | | | | 4.6 | 1.8 | -5 | | | | | |
| | | | $H^+$ = 0.16; $I^-$ = 0.16 | | | | 10.4 | 3.6 | -5 | | | | | |
| | | | | | | | 15.0 | 6.0 | -5 | | | | | |
| | | | | | | | 20.0 | 9.7 | -5 | 17.0 | | | | |
| .8.1 | $H_3AsO_3 + HIO \rightarrow H_3AsO_4 + I^- + H^+$ | $H_2O$ | " | " | | $k\,AB$ | 0 | 2.3 | -1 | ~ 0 | | | * | " |
| .9 | $3\,AsO_3^{---} + IO_3^- \rightarrow 3\,AsO_4^{---} + I^-$ | $H_2O$ | B = 0.001 | $10^5[H^+]$ = 2 - 4 | | $k\,B[H^+]^2[I^-]^2$ | | | | | | | * | (9) (21) |
| | | | $I^-$ = 0.02 - 0.04 | | | | 25 | 1.7 | 9 | | | | | |
| .10 | $AsO_2^- + IO_4^- \rightarrow AsO_3^- + IO_3^-$ | $H_2O$ | $CH_3COOH + CH_3COO^-$ buffer | | | $k\,AB$ | 25 | 9.2 | -2 | | | | | (1) |

## COMMENTS

(.1) Assumed mechanism $NO_2^- + I_2 \rightarrow NO_2 + I^- + I$ ($k_1$); $NO_2 + I^- + I \rightarrow NO_2^- + I_2$ ($k_2$); $NO_2 + I \rightarrow NO_2 + I^-$ ($k_3$); $NO_2 + I^- \rightarrow NO_2 + I$ ($k_4$); $2\,NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ ($k_5$); $K = [I^-][I_2]/[I_3^-]$ = 0.00225 at 50° and 0.0026 at 60°C; $k = k_1K$; $a = k_2k_4/k_3k_5$. (.2) Proposed mechanism $N_3^- + CS_2 \rightarrow SCSN_3^-$ (rate determining); $2\,SCSN_3^- + I_2 \rightarrow (SCSN_3)_2 + 2\,I^-$; $(SCSN_3)_2 + 2\,N_3^- \rightarrow 2\,CS_2 + 2\,N_3^- + 3\,N_2$. (.3) Propanol (up to 7 %) added to inhibit the reaction between $HIO_3$ and HI; AgCl added to eliminate $I^-$. Mechanism assumed $n - H_3PO_2 \rightarrow a - H_3PO_2$ (normal → active) ($k_1$); $a - H_2PO_2 \rightarrow n - H_3PO_2$ ($k_2$); $a - H_3PO_2 + IO_3^- \rightarrow$ products ($k_3$); $k = k_1$; $k' = k_2/k_3$. Reaction 3 is about 1/35 as fast as oxidation of $a - H_3PO_2$ by halogens or by $Hg^{++}$. Reactions 1, 2, are acid-catalyzed. See further (14) (5) (6). (.4) (.4.1) (.4.2) (.4.3) Reaction (.4.1) is predominant in (.4) at pH > 6, or at or above 50°C; the rate of (.4) is then represented by the equation given under (.4), in terms of the rate constant $k_1$, of (.4.1) and of $K = [I^-][I_2]/[I_3^-]$ = 0.00155 at 30°C. The acid-catalyzed reaction $H_2PO_2^- + H^+ \rightarrow a - H_3PO_2$ (active) is negligible at

## COMMENTS *(continued)*

pH < 3.4. The acid-catalyzed reaction $n - H_3PO_2$ (normal) $+ H^+ \rightarrow H_3PO_2.H^+$ is favored at high $[H^+]$. At pH >> 3.4, the follow-up reaction is (.4.2) or (.4.3); the second-order rate constants for the reactions $a - H_3PO_2 + I_2 + H_2O$ and $a - H_3PO_2 + I_3^-$ are, respectively, $k_2/K$ and $k_3/K$, where $K = a - H_3PO_2/n - H_3PO_2$. (.5) (.5.1) (.5.2) (.5.3) (.5.4) Selected empirical data; further data in acetate and chloroacetate buffers, see original ([5]). Significant steps of the overall reaction are, (.5.1), acid-catalyzed, and followed by $H_3PO_3.H^+ + \text{base} \rightarrow a - H_3PO_3$ (active); this is followed by $a - H_3PO_3 + I_2 + H_2O$ (.5.3) or $a - H_3PO_3 + I_3^- + H_2O$ (.5.4). The rate constants of the reactions $a - H_3PO_3 + I_2 + H_2O$ and $a - H_3PO_3 + I_3^- + H_2O$ are, respectively, $k_3/K$ and $k_4/K$ [see comment (.4)]. At higher pH, the significant step is (.5.2), whereas $H_2PO_3^- + I_2 + H_2O$ is negligible. (.6) In concentrated HCl, the order is higher than $[H^+]^2$. The rates are independent of $H_3AsO_3$ which acts only to eliminate the products. The rate determining steps are $X^- + XO_3^- + 6\,H^+ \rightarrow 3\,X_2 + 3\,H_2O$ (see 722.770); X = Cl, Br, I. The acceleration by $H_3AsO_4$ (with Br, I) is interpreted by $2\,X^- + 2\,H^+ + H_3AsO_4 \rightleftarrows X_2 + H_3AsO_3$; $X_2 + 2\,ClO_3^- \rightarrow Cl_2 + 2\,XO_3^-$; $H_3AsO_3 + Cl_2 + H_2O \rightarrow H_3AsO_4 + 2\,Cl^- + 2\,H^+$; $3\,H_3AsO_3 + XO_3^- \rightarrow 2\,H_3AsO_4 + X^-$. (.7) Rate independent of $H_3AsO_3$, as above (.6). Rate determining step, $5\,Cl^- + BrO_3^- + 6\,H^+ \rightarrow 2\,Cl_2 + BrCl + 3\,H_2O$ (see 722.770). (.8) Mechanism ([10])([15])([11])([2]) $I_2 + H_2O \rightleftarrows HIO + I^- + H^+$, fast; $H_3AsO_3 + HIO \rightleftarrows H_4AsIO_4$, fast; $H_4AsIO_4 \rightarrow H_3AsO_4 + I^- + H^+$. (.8.1) Derived from (.8); $[I_3^-]/[I_2][I^-] = 1/7.2 \times 10^{-4}$ and $[I_2] = [H^+][I^-][HIO]/9 \times 10^{-5}$. (.9) The fifth-order Dushman reaction goes over partly into a fourth-order reaction $A[H^+]^2[I^-]$ with decreasing $[I^-]$, and consequently $k$ decreases. If $I^-$ is added at the start, the reaction $5\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$ is followed by $AsO_3^{---} + I_2 + H_2O \rightarrow AsO_4^{---} + 2\,I^- + 2\,H^+$, rapid until equilibrium is approached. See further ([18]) (criticism), ([3]) ([16]).

## LITERATURE

(1) E. Abel, K. Fürth, *ZPC* 1923, **107**, 305. (2) N. C. Bray, *CRV* 1932, **10**, 165. (3) G. G. Durrant, R. O. Griffith, A. McKeown, *TFS* 1936, 32, 999. (4) J. Eggert, B. Scharnon, *ZEC* 1921, **27**, 464. (5) R. D. Griffith, A. McKeown, *TFS* 1940, 36, 766. (6) R. D. Griffith, A. McKeown, R. P. Taylor, *TFS* 1940, **36**, 752. (7) P. Haywood, D. M. Yost, *ACS* 1949, **71**, 915. (8) N. Hofman-Bang, W. Szybalski, *ACS* 1949, 3, 1418. (9) H. Kubina, *MHC* 1922, **43**, 439. (10) H. A. Liebhafsky, *JPC* 1931, 35, 1648.

(11) H.A.Liebhafsky, *ZPC* 1931, **155**, 289. (12) H. A. Liebhafsky, *ACS* 1939, **61**, 3513. (14) A. D. Mitchell, *CSL* 1920, **117**, 1322. (15) J. R. Roebuck, *JPC* 1902, **6**, 365; 1905, **9**, 727. (16) R. P. Sanyal, N. R. Dhar, *ZAC* 1924, **139**, 169. (17) A. Skrabal, Homogenkinetik 119-123, Steinkopff, Dresden and Leipzig, 1941. (18) A. Skrabal, Rieder, *ZEC* 1924, 30, footnote p. 113. (19) A. Skrabal, H. Schreiner, *MHC* 1922, 43, 439. (20) A. Skrabal, H. Schreiner, MHC 1935, 65, 213.

(21) A. Skrabal, A. Zahorka, *ZEC* 1927, 33, 43-44.

# OXIDATION-REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** V th group element

**Oxidant:** VIII th group (or rare earth) element

Rates are in units of amounts per sec.

| No. | Reaction | Solvent | Unit of amount | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $NO_2^- + Fe^{+++} \rightarrow NO_2 + Fe^{++}$ | $H_2O$ | M/l | | | | $k\,AB$ | 25 | 1.0 | 0 | * | (1) |
| .2 | $AsO_3^{---} + 2\,Ce^{++++} + H_2O \rightarrow AsO_4^{---} + 2\,Ce^{+++} + 2\,H^+$ | $H_2O$ | equiv/l | A = 0.025; B = 0.05 | $H_2SO_4$ | 1 | $k\,AB^2$ | 30 | 3.1 | −1 | * | (2, 3) |
| | | | | " 0.025 | | | | " | 4.4 | −1 | | |
| | | | | " 0.125 | | | | " | 5.1 | −1 | | |
| | | | | 0.0125 0.05 | | | | " | 3.0 | −1 | | |
| | | | | " 0.025 | | | | " | 4.3 | −1 | | |
| | | | | 0.00625 0.05 | | | | " | 1.1 | −1 | | |

## COMMENTS

(.1) Derived from the reaction $Fe^{++} + HNO_2 + H^+ \rightarrow Fe^{+++} + NO + H_2O$. Since NO reacts by $NO + NO_2 + H_2O \rightarrow 2\,HNO_2$, this reaction is virtually the reverse of $Fe^{++} + HNO_2 + H^+ \rightarrow Fe^{+++} + NO + H_2O$. (.2) The third-order $k$ increases with decreasing B and with increasing A; $k$ increases on addition of $H_2SO_4$, $HNO_3$, $HClO_4$, in that order. The mechanism of (3) $AsO_2^- + Ce^{++++} \rightarrow Ce^{+++} + AsO_2$ is criticized by (2) as calling for second order (not verified) and postulating $AsO_2$. Activation energies (2), in A = 0.025, B = 0.05, $H_2SO_4$ = 1.0, $E$ = 21; in A = 0.00625, B = 0.05, $H_2SO_4$ = 2.0, $E$ = 17; according to (3), $E$ varies from 9.5 in $HClO_4$ to 17.0 in $H_2SO_4$.

## LITERATURE

(1) E. Abel, H. Schmid, F. Pollak, *MHC* 1936, **69**, 141. (2) J.W. Moore, R.C. Anderson, *ACS* 1944, **66**, 1476. (3) N. F. Stefanovskii, M. S. Gaukhman, *ZhOKh* 1941, **11**, 970.



942151 O—51——46

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** VI th group

**Oxidant:** " " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Ionic Strength | Addend (Catalyst) | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ $k^0$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $Cr^{+++} + S_2O_8^{--} + 7\ H_2O \rightarrow Cr_2O_7^{--} + 6\ SO_4^{--} + 14\ H^+$ | $H_2O$ | $\mu = 0.234$ | $Ag^+$ | $k B [Ag^+]$ | 25 | 5.7 | -3 | |
| | | | | | | 35 | 1.3 | -2 | 15 |
| | | | 0.485 | " | " | 25 | 5.3 | -3 | |

## COMMENTS

The rate is independent of $[Cr^{+++}]$. Rate determining step $Ag^+ + S_2O_8^{--} \rightarrow Ag^{+++} + 2\ SO_4^{--}$, followed by $3\ Ag^{+++} + 2\ Cr^{+++} + 7\ H_2O \rightarrow 3\ Ag^+ + Cr_2O_7^{--} + 14\ H^+$, fast.

## LITERATURE

D.M. Yost, *ACS* 1926, **48**, 152.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** VI th group element

**Oxidant:** VII th " "

Amounts are in M/l.

Rates in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | Completion time | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $SO_3^{--} + I_2 + H_2O \rightarrow SO_4^{--} + 2\,I^- + 2\,H^+$ | $H_2O$ | A = B = 0.09 | HCl | 1 | | 0 | 20 | | | | * | (8)(3) |
| | | | | | | | ~ 20 | 4 | | | | | |
| | | | | | 2 | | 0 | 360 | | | | | |
| | | | | | | | ~ 20 | 15 | | | | | |
| | | | | $H_2SO_4$ | 0.5 | | 0 | 18 | | | | | |
| | | | | | | | ~ 20 | 4 | | | | | |
| | | | | | 1 | | 0 | 420 | | | | | |
| | | | | | | | ~ 20 | 14 | | | | | |
| .2 | $3\,SO_3^{--} + IO_3^- \rightarrow 2\,SO_4^{--} + I^-$ | $H_2O$ | B = 0.003 - 0.02; | $kA$; | $k = k_1B[HSO_3^-][H^+] + k_2A^2B[H^+]^2$ | | | | | | | * | (7) |
| | | | A = 3B; pH = 7 - 9 | | | | 25 | $k_2$ | 1.1 | +15 | | | |
| .2.1 | $2\,HSO_3^- + IO_3^- + CH_3COO^- \rightarrow 3\,SO_4^{--} + I^- + 3\,CH_3COOH$ | $H_2O$ | $10^3A = 1.5 - 9$<br>$10^4B = 5 - 10$<br>pH = 4 - 5 | | | $k_1AB[H^+]$ | 25 | $k_1$ | 8.8 | +3 | | * | " |
| .3 | $6\,S_2O_3^{--} + IO_3^- + 6\,H^+ \rightarrow 3\,S_4O_6^{--} + I^- + 3\,H_2O$ | $H_2O$ | $10^2A = 1 - 6$<br>$10^3B = 2 - 15$<br>$10^5[H^+] = 2$ | | | $kA^2B\,[H^+]^2$ | 24(34?) | | 5.0 | 8 | 4.7 | * | (4)(1) |

## COMMENTS

(.1) The retardation at high $[H^+]$ suggests that $OH^-$ is involved. (.2) (.2.1) The main reaction (.2), with the rate constant $k_2$, is isolated only between pH 7 and 9, and when $[SO_3^{--}]$ is relatively large or $[I^-]$ very small (as in the presence of AgCl). The special case (.2.1), with the rate constant $k_1$, is isolated between pH 4 and 5 only. At pH 13, the reaction is too slow to measure. When $[H^+] \geqq 0.01$, $HIO_3$ reacts so fast that the iodine-sulfite reaction becomes rate determining. If $I^-$ is added at the start, the reaction $IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$ becomes rate determining. (.3) The rate equation corresponds to Dushman's fifth-order reaction $5\ I^- + IO_3^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$ (rate determining), followed by the rapid reaction $2\ S_2O_3^{--} + I_2 = S_4O_6^{--} + 2\ I^-$. The rate of the Dushman reaction is increased in the presence of $S_2O_3^{--}$. The temperature coefficient agrees with the Dushman reaction ( A.Skrabal, *Gmelin Handbuch*, 8th edition, System-number 8, p. 569). See further (4) (5).

## LITERATURE

(1) J.Eggert, L.Pffermann, *ZAC* 1924, **139**, 310. (2) J.Eggert, B.Scharnow, *ZEC* 1921, **27**, 455. (3) A.W.Francis, *ACS* 1926, **48**, 655. (4) R.Rieder, *JPC* 1930, **34**, 2111. (5) W.Roman-Levinson, *ZEC* 1928, **34**, 333. (6) A.Skrabal, *ZEC* 1922, **28**, 224. (7) A.Skrabal, A.Zahorka, *ZEC* 1927, **33**, 48. (8) A.Thiel, E.Meyer, *ZAC* 1924, **137**, 138.

# OXIDATION-REDUCTION

## of compounds of different elements

**Reductant:** VII th group element

**Oxidant:** $H_2O_2$

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Addend (catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ | $H_2O$ | HBr | 0.01 - 0.38 | $A(k_1[H^+][Br^-] + k_2[Br_2]/[H^+][Br^-])$ | | | | | | | * | * |
| | | | See reactions (.1.1), (.1.2) | | | | | | | | | | |
| .1.1 | $Br^- + H_2O_2 + H^+ \rightarrow HBrO + H_2O$ | $H_2O$ | HBr | 0.01 - 0.38 | $k_1ABC$ | 25 | 3.6 | -4 | | | | * | * |
| .1.2 | $HBrO + H_2O_2 \rightarrow Br^- + H^+ + H_2O$ | $H_2O$ | HBr | 0.01 - 0.38 | $k_2A[Br_2]/[H^+][Br^-]$ | | | | | | | | |
| | | | | | | 0 | 1.03 | -5 | | | | * | * |
| | | | | | | 25 | 3.0 | -4 | | | | | |
| | | | | | | 35 | 7.1 | -4 | | | | | |
| .2 | $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ | $H_2O$ | HI | See reactions (.1.1) (.2.2) | | | | | | | | * | * |
| .2.1 | $3\,I^- + H_2O_2 + 2\,H^+ \rightarrow I_3^- + 2\,H_2O$ | $H_2O$ | | | $k_1AB + k_1'AB[H^+]$ | 25 | | | | | | * | * |
| | | | | | | $k_1$ | 1.15 | -2 | 13.4 | 8.2 | 7 | | |
| | | | | | | $k_1'$ | 1.75 | -1 | 10.4 | 7.6 | 6 | | |
| .2.1[a] | $I^- + H_2O_2 \rightarrow IO^- + H_2O$ | $H_2O$ | | | $k_1AB$ | 25 | 1.15 | -2 | 13.4 | 8.2 | 7 | * | * |
| .2.1[b] | $I^- + H_2O_2 + H^+ \rightarrow HIO + H_2O$ | $H_2O$ | | | $k_1'AB[H^+]$ | 25 | 1.75 | -1 | 10.4 | 7.6 | 6 | * | * |
| .2.2 | $H_2O_2 + I_2 \rightarrow 2\,H^+ + 2\,I^- + O_2$ | $H_2O$ | | | $AB(k_2/[I^-][H^+]^2 + k_2'/[I^-][H^+])$ | | | | | | | * | * |
| | | | | | | 25 | | | | | | | |
| | | | | | | $k_2$ | 2.0 | -14 | | | | | |
| | | | | | | $k_2'$ | 1.1 | -11 | | | | | |

| No. | Reaction | Solvent | Addend (catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2.2[a] | $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ | $H_2O$ | | | $k_{2a}AB$ | 25 | 3.3 | +9 | | | | * | * |
| .2.2[b] | $H_2O_2 + HIO \rightarrow H_2O + H^+ + I^- + O_2$ | $H_2O$ | | | $k_{2b}AB$ | 25 | 3.7 | +1 | | | | * | * |
| .3 | $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ | $H_2O$ | NaI | 0.0205 | $kA$ | 25 | 5.0 | -4 | | | | | (4) |
| | | $H_2O + CH_3OH$ 24 % | " | " | | " | 2.7 | -4 | | | | | |
| | | 46 | | " | | " | 1.7 | -4 | | | | | |
| | | 93.5 | | " | | " | 9.5 | -5 | | | | | |
| | | $H_2O + C_2H_5OH$ 32.6 % | " | " | " | 25 | 2.1 | -4 | | | | | |
| | | 56 | | " | | " | 1.7 | -4 | | | | | |
| | | 93.4 | | " | | " | 1.7 | -4 | | | | | |
| | | $H_2O + C_3H_7OH$ 28.3 % | " | " | " | 25 | 3.0 | -4 | | | | | |
| | | 93.9 | | | | " | 5.5 | -4 | | | | | |
| | | $H_2O + i\text{-}C_4H_9OH$ 93.4 % | " | " | | 25 | 1.5 | -3 | | | | | |
| | | $H_2O + C_5H_{11}OH$ 93.5 | " | " | | 25 | 2.1 | -3 | | | | | |
| | | $H_2O + C_3H_5(OH)_3$ 95.7 | " | " | | " | 1.4 | -3 | | | | | |
| | | $H_2O + C_5H_5N$ 33.5 % | " | 0.1026 | | " | 1.1 | -3 | | | | | |
| | | 67.1 | | " | | " | 2.8 | -4 | | | | | |
| | | 81.7 | | " | | " | 1.5 | -4 | | | | | |
| | | 94.7 | | " | | " | 2.7 | -4 | | | | | |
| .4 | $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ | $H_2O$ | KI | 0.02 | $kA\,[I^-]$ | 15 | 1.0 | -2 | | | | * | (10) |
| | | | | | | 25 | 2.3 | -2 | | | | | (23) |
| | | | | | | 35 | 4.7 | -2 | | | | | |
| | | | | | | 45 | 9.6 | -2 | 13.8 | | | | |

| No. | Reaction | Solvent | Addend (catalyst) | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ *(continued)* | $H_2O + CH_3OH$ 25.5 % | KI | 0.02 | $k\,A[I^-]$ | 15 | 5.3 | -3 | | | | | ([10]) |
| | | " " | | | | 25 | 1.2 | -2 | | | | | ([23]) |
| | | " " | | | | 35 | 2.7 | -2 | | | | | |
| | | " " | | | | 45 | 6.0 | -2 | 15.1 | | | | |
| | | " 54.4 | " | " | " | 15 | 2.8 | -3 | | | | | " |
| | | " " | | | | 25 | 7.0 | -3 | | | | | |
| | | " " | | | | 35 | 3.3 | -2 | | | | | |
| | | " " | | | | 45 | 3.8 | -2 | 15.8 | | | | |
| | | $CH_3OH$ 100 % | " | " | " | 15 | 1.6 | -3 | | | | | " |
| | | | | | | 25 | 4.4 | -3 | | | | | |
| | | | | | | 35 | 1.1 | -2 | | | | | |
| | | $H_2O$ | KI 0.02 | + NaCl 1 | " | 15 | 1.2 | -2 | | | | | |
| | | | | | | 25 | 2.7 | -2 | | | | | |
| | | | | | | 35 | 5.6 | -2 | | | | | |
| | | | | | | 45 | 1.15 | -1 | 13.7 | | | | |
| .5 | $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ | $H_2O$ | $CdI_2$ | 0.005 - 0.5 | $A(k_1[I^-] + k_2[CdI^+] + k_3[CdI_3^-])$ | | | | | | | * | ([9]) |
| | | | | | | 25 | | | | | | | |
| | | | | | | $k_1$ | 2.6 | -2 | | | | | |
| | | | | | | $k_2$ | ~ 1.0 | -2 | | | | | |
| | | | | | | $k_3$ | ~ 1.3 | -2 | | | | | |
| | | " | KI | 0.005 - 0.1 | $k\,A\,[I]$ | 25 | 2.4 | -2 | | | | | |

## COMMENTS

**(.1) (.1.1) (.1.2)** Reaction (.1), catalyzed by the $Br^- + Br_2$ couple, proceeds over the steps (.1.1) and (.1.2). The data of $k_1$ and $k_2$ refer to mass action expressed in activities, i.e. $k_1 = k'_1 / f^2$ and $k_2 = k'_2 / f^2$, where $k'_1$ and $k'_2$ are the concentrational rate constants, $f$ = activity coefficient of HBr. The concentration of HBrO in the overall reaction is stationary. Literature (19) (1) (5) (12) (13) (14) (16) (2)

**(.2) (.2.1) (.2.2)** Reaction (.2), catalyzed by the $I^- + I_2$ couple, proceeds over the steps (.2.1) [ which proceeds over (.2.1[a]) and (.2.1[b])]; $k_2$ and $k'_2$ are with $[H^+]$ expressed in activities. The relations between the constants are, $k_{2a} = k_2 / K_a$, where $K_a = [HIO][H^+][I^-] / [I_2] = 6 \times 10^{-24}$; $k_{2b} = k'_2 / K_b$, where $K_b = [IO^-][H^+]^2 [I^-] / [I_2] = 3 \times 10^{-13}$. Literature (3) (6) (7) (17) (18) (15) (20) (8)

**(.3) (.4) (.5)** Reactions catalyzed by the $I^- + I_2$ couple. Catalytic constant defined by $kA[I^-]$, at 25°C, in fairly good agreement $\sim 2.4 \times 10^{-2}$. **(.4)** Data on further salt effects, KBr, $K_2SO_4$, $MgSO_4$, $BaCl_2$, in original (10). Calculations based on triple collisions predict $k$ values in fair agreement with the experiment. **(.5)** Only $I^-$, $CdI^+$, and $CdI_3^-$ have a catalytic effect; $Cd^{++}$ has none. Addition of $I_2$ to $CdI_2$ 0.125 – 0.250 has little effect, but $I_2$ added to $CdI_2 < 0.0075$ decreases $k$ rapidly. See further (21) (22) (11).

## LITERATURE

(1) E. Abel, *ZPC* 1928, **136**, 161. (2) E. Abel, L. Blumenkranz, *MHC* 1935, **66**, 187 (footnote). (3) Balint, *Thesis, Univ. Budapest.* (4) V.L. Bohnson, *JPC* 1920, **24**, 677. (5) W. C. Bray, H. A. Liebhafsky, *ACS* 1931, **53**, 38. (6) W. C. Bray, R. S. Livingston, *ACS* 1923, **45**, 1251. (7) W. C. Bray, R. S. Livingston, *ACS* 1928, **50**, 1654. (8) J. A. Christiansen, *ZPC* 1925, **117**; 453; 1927, **128**, 430. (9) R. U. Gooding, J. H. Walton, *JPC* 1931, **35**, 3612. (10) W. C. Hender, R.A. Robinson, *TFS* 1933, **29**, 1300.

(11) M. E. Laing, J W. McBain, *JPC* 1924, **28**, 673. (12) H. A. Liebhafsky, *ZPC* 1931, **155**, 289. (13) H. A. Liebhafsky, *ACS* 1932, **54**, 1792. (14) H. A. Liebhafsky, *ACS* 1932, **54**, 3499, 3509.

## LITERATURE *(continued)*

(15) H. A. Liebhafsky, *ACS* 1939, **61**, 3514. (16) H. A. Liebhafsky, A. Mohammad, *ACS* 1933, **55**, 3977.

(17) R. S. Livingston, W. C. Bray, *ACS* 1923, **45**, 2048. (18) R. S. Livingston, *ACS* **48**, 53.

(19) G. Magnanini, *GCI* 1891, **21**, 746. (20) B. Makower, H. A. Liebhafsky *TFS* 1933, **29**, 57.

(21) J. W. McBain, *ZEC* 1905, **11**, 215. (22) J. W. McBain, *JPC* 1931 **35**, 999.

(23) E. A. Moelwyn-Hughes, A. P. Legard, *CSL* **1933**, 424.

# OXIDATION-REDUCTION

## of compounds of different elements

**Reductant:** **VII$^{th}$ group element**

**Oxidant:** **ozone**

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend (Catalyst) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | $A = A^o \times 10^n$ $A^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ Cl^- + O_3 + 2\ H^+ \rightarrow Cl_2 + O_2 + H_2O$ | $H_2O$ | A = 0.02 - 0.1<br>B = 0.0004 - 0.004 | $Co^{++}$ = 0.00011 - 0.00044 | $k_1AB + k_2AB[H^+] + k_3B[Co^{++}]$ | 0 | | | | | |
| | | | | | | $k_1$ | 2.1 | -4 | 17.6 | 2.3 | 10 |
| | | | | | | $k_2$ | 2.1 | -3 | 17.5 | 2.0 | 11 |
| | | | | | | $k_3$ | 6.6 | -1 | (0-9.5°C) | | |

## COMMENTS

Spontaneous decomposition of $O_3$ slight; $Cu^{++}$ and $Fe^{+++}$ are without measurable effect. Mechanism for $k_1$, $Cl^- + O_3 \rightarrow ClO^- + O_2$, rate determining; $ClO^- + Cl^- + 2\ H^+ \rightarrow Cl_2 + H_2O$, fast. For $k_3$, $Co^{++} + O_3 + H_2O \rightarrow COOH^+ + O_2 + OH$, rate determining.

## LITERATURE

Le R. B. Yeatts, Jr., H. Taube, *ACS* 1949, **71**, 4100.

# OXIDATION-REDUCTION
## of compounds of different elements

*Liquid phase*

**Reductant:** VII th group element
**Oxidant:** V th " "

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $3\,I^- + H_3AsO_4 + 2\,H^+ \rightarrow I_3^- + H_3AsO_3 + H_2O$ | $H_2O$ | $k\,ABC$ | 0 | 1.05 | -4 | | * | (1) (2) (4) (5) |
| | | | | 25 | 1.2 | -3 | 14.1 | | |
| .2 | $3\,I^- + 2\,V(OH)_4^+ + 4\,H^+ \rightarrow I_3^- + 2\,VO^{++} + 6\,H_2O$ | $H_2O$ | $k\,ABC^2$ | 25 | 1.3 | -1 | | * | (3) |

## COMMENTS

(.1) Calculated (5) from exchange of radioactive $As^{76}$ between $AsO_3^{---}$ and $AsO_4^{---}$ in the presence of $I_3^-$ and $I^-$ (no exchange in their absence). Mechanism represented as $A + B + C \rightarrow H_4AsIO_4$, fast; $H_4AsIO_4 \rightarrow I_3^- + HIO$, rate determining; $HIO + 2\,I^- + 2\,H^+ \rightarrow I_3^- + H_2O$, fast. (.2) The plot of $-d\ln B/dt$ against $k\,AC^2$ is linear.

## LITERATURE

(1) H. A. Liebhafsky, *JPC* 1931, **35**, 1648. (2) H.A. Liebhafsky, *ACS* , 1939, **61**, 3515.

(3) J. B. Ramsey, E. L. Colichman, L. C. Pack, *ACS* 1946, **68**, 1695. (4) J.R.Roebuck *JPC* 1902, **6**, 365; 1905, **9**, 727. (5) J.N. Wilson, R. G. Dickinson, *ACS* 1937, **59**, 1358.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** VII th group element

**Oxidant:** VI th " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\,I^- + S_2O_8^{--} \rightarrow I_2 + 2\,SO_4^{--}$<br>$2\,I_3^- + S_2O_8^{--} \rightarrow 3\,I_2 + 2\,SO_4^{--}$ | $H_2O$ | $I^- = 0.01$<br>$B = 0.005$<br>$\mu = 0.025$ | $-dB/dt = k_1[I^-]B + k_2[I_3^-]B$ | | | 25 | | | | (2) |
| | | | | | | | $k_1$ | 2.1 | -3 | | |
| | | | | | | | $k_2$ | 1.07 | -3 | | |
| | | " | $I^- = 0.025$; $B = 0.0125$ | X = | 0.0001 - 0.0005 | $k[I^-]B + k'B[X]$ | | | | * | (4) |
| | | | | | | | 25 | | | | |
| | | | | $Fe^{++}$ | | | $k'$ | 9.1 | 0 | | |
| | | | | $Cu^{++}$ | 0.0001 | " | $k'$ | 7.8 | 0 | | |
| | | | | | 0.0002 | | | 5.8 | 0 | | |
| | | | | | 0.0005 | | | 4.6 | 0 | | |
| .2 | $6\,I^- + Cr_2O_7^{--} + 14\,H^+ \rightarrow 3\,I_2 + 2\,Cr^{+++} + 7\,H_2O$ | $H_2O$ | $10^4A = 68 - 277$;<br>$10^4B = 2.0$<br>$10^4[H^+] = 176 - 531$ | NaCl | 1.5 | $kB$; $k = aA[H^+] + bA^2[H^+]$ | | | | | |
| | | | | | | | 25 | | | * | (1) |
| | | | | | | | $a$ | 2.4 | -1 | | |
| | | | | | | | $b$ | 8.9 | +2 | | |



94151 O—51——47

## COMMENTS

(.1) The mechanisms of the catalyzed reaction are formulated $Fe^{++} + S_2O_8^{--} \longrightarrow FeS_2O_8$ (rate determining); $FeS_2O_8 \longrightarrow 2\ Fe^{+++} + 2\ SO_4^{--}$, fast; $2\ Cu^{++} + 2\ I^- \longrightarrow 2\ Cu^+ + I_2$, fast; $Cu^+ + S_2O_8^{--} \longrightarrow CuS_2O_8^-$, rate determining ($k'$); $Cu^+ + CuS_2O_8^- \longrightarrow 2\ Cu^{++} + 2\ SO_4^{--}$, fast. (.2) The rate law holds only at the given concentrations; otherwise the rate is $k$ABC or $k$AB$^2$C$^2$; $k$ passes through a minimum at $\mu = 0.5$, and is about equal at $\mu = 0.04$ and $\mu = 1.5$.

## LITERATURE

(1) R. F. Beard, N. W. Taylor, *ACS* 1929, **51**, 1973. (2) E. Jette, C. V. King, *ACS* 1929, **51**, 1034, 1048. (3) E. Jette, C. V. King, *ACS* 1929, **51**, 1039. (4) A. von Kiss, L. von Zombory, *RTC* 1927, **46**, 225.

# OXIDATION-REDUCTION

## of compounds of different elements

**Reductant:** VII$^{th}$ group element

**Oxidant:** VII$^{th}$ group element

*Liquid phase*

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $5\ Cl^- + BrO_3^- + 6\ H^+ \rightarrow 2\ Cl_2 + BrCl + 3\ H_2O$ | $H_2O$ | $H_3AsO_3$ | $k\ ABC^2$ | 25 | 1.5 | −3 | * | ([6]) |
| .1.1 | $5\ Cl^- + BrO_3^- + 6\ H^+ \rightarrow 2\ Cl_2 + BrCl + 3\ H_2O$ | $H_2O$ | | $k\ ABC^2$ | 25 | 5.3 | −1 | * | ([1]) ([8]) |
| | | $D_2O$ | | " | " | 1.9 | 0 | | " |
| .2 | $6\ Br^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + Cl^- + 3\ H_2O$ | $H_2O$ | $HNO_3$ | $k\ ABC^2$ | 40 | 1.0 | −5 | * | ([4]) |
| .2.1 | $6\ Br^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + Cl^- + 3\ H_2O$ | $H_2O$ | $H_3AsO_3$ | $k\ ABC^2$ | 25 | 1.5 | −6 | * | ([7]) |
| .3 | $6\ I^- + ClO_3^- + 6\ H^+ \rightarrow 3\ I_2 + Cl^- + 3\ H_2O$ | $H_2O$ | | $k\ ABC^2$ | 30 | 1.8 | −5 | * | ([2]) ([3]) |
| .3.1 | $6\ I^- + ClO_3^- + 6\ H^+ \rightarrow 3\ I_2 + Cl^- + 3\ H_2O$ | $H_2O$ | $H_3AsO_3$ | $k\ ABC^2$ | 25 | 3.3 | −5 | * | ([7]) |

## COMMENTS

(.1) Derived from $3\ H_3AsO_3 + BrO_3^- \rightarrow 3\ H_3AsO_4 + Br^-$, in the presence of HCl. (.1.1) Measured in 91 % $D_2O$, extrapolated to 100 % $D_2O$. (.2) ([5]) predicted $k = 8.2 \times 10^{-6}$ at 25°C. (.2.1) Derived from $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$, in the presence of HBr. (.3) Ten-degree temperature coefficient = 2.6. (.3.1) Derived from $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$, in the presence of HI.

## LITERATURE

(1) E. Abel, F. Fabian, *MHC* 1938, 71, 153. (2) W. C. Bray, *JPC* 1903, 7, 92. (3) W. C. Bray, *ZPC* 1908, 54, 463. (4) J. Hirada, *Bull. Chem. Soc. Japan* 1935, 10, 97. (5) A. Skrabal, R. Rieder, *ZEC* 1924, 30, 109. (6) A. Skrabal, H. Schreiner, *MHC* 1922, 43, 439. (7) A. Skrabal, H. Schreiner, *MHC* 1935, 65, 213. (8) A. Skrabal, S. R. Weberitsch, *MHC* 1915, 36, 211.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

Reductant: VII th group element

Oxidant: VIII th " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Ionic strength | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\,I + 2\,Fe^{+++} \rightarrow I + 2\,Fe^{++}$ | $H_2O$ | $\mu =$ | $-dB/dt = r_1 + r_2$ | 25 | | | * | (2)(3) |
| | (nitrates) | | 0.09 | $r_1 = k_1A^2B/\{1 + M/B(m_4 + m_6A)\}$ | $k_1$ | 8.7 | +1 | | (4)(10) |
| | | | | | $m_4$ | 1.8 | -2 | | |
| | | | | | $m_6$ | 2.0 | +1 | | |
| | | | 0 | | $k_1$ | 8.1 | +2 | | |
| | | | | | $m_4$ | 2.8 | -1 | | |
| | | | | | $m_6$ | 7.5 | +1 | | |
| | | | | $r_2 = k_1'AB/(1 + M[H^+]/Bm')$ | | | | | |
| | | | 0.09 | | $k_1'$ | 1.2 | -2 | | |
| | | | | | $m'$ | 1.4 | -3 | | |
| | | | 0 | | $k_1'$ | 4.3 | -2 | | |
| | | | | | $m'$ | 3.4 | -3 | | |



94510 O-51——48

## COMMENTS

Reverse reaction, see 732.870. The forward and the reverse reactions are interpreted by a scheme (one variant):

$Fe^{+++} + I^- \rightleftharpoons FeI^{++}$ (fast, $K_2$); $FeI^{++} + I^- \rightarrow Fe^{++} + I_2^-$ ($1/2k_1/K_2$); $Fe^{++} + I_2^- \rightarrow FeI^{++} + I^-$ ($k_2$);

$Fe^{+++} + I_2^- \rightarrow Fe^{++} + I_2$ ($k_3$); $Fe^{++} + I_2 \rightarrow Fe^{+++} + I_2^-$ ($1/2k_4$); $FeI^{++} + I_2^- \rightarrow Fe^{++} + I_3^-$ ($k_5/K_2$);

$Fe^{++} + I_3^- \rightarrow FeI^{++} + I_2^-$ ($1/2k_6$); $Fe^{++} + H_2O \rightarrow Fe^{++} + IOH^- + H^+$ ($1/2k_1/K_2$); $Fe^{++} + IOH^- + H^+ \rightarrow$

$Fe^{++} + H_2O$ ($k_2'$); $Fe^{+++} + IOH^- \rightarrow Fe^{++} + IOH$ ($k_3'$); $Fe^{++} + IOH \rightarrow Fe^{+++} + IOH^-$ ($1/2k_4'/K_3$);

$IOH + I^- + H^+ \rightleftharpoons I_2 + H_2O$ (fast, $1/K_3$); $m_4 = k_3/k_2$; $m_6 = k_5/k_4$; $m' = k_3'/k_2'$;

$K = [Fe^{++}]^2[I_2]/[Fe^{+++}]^2[I^-]^2$. Further literature references (1) (5) (6) (7) (8) (9).

## LITERATURE

(1) R.C.Banerji, N.R.Dhar, *ZAC* 1924, **134**, 172. (2) W.C.Bray, M.H.Gorin, *ACS* 1932, **54**, 2124.

(3) A.V.Hershey, W.C.Bray, *ACS* 1936, **58**, 1760. (4) N.Sasaki, *ZAC* 1924, **137**, 181. 291.

(5) K.Tominaga, S.Toraiski, *C.A.* 1931, **25**, 5613. (6) A.von Kiss, *C.A.* 1931, **25**, 2631.

(7) A.von Kiss, *ZAC* 1931, **198**, 102. (8) A.von Kiss, I.Bossanyi, *ZAC* 1930, **191**, 289.

(9) A.von Kiss, I.Bossanyi, *C.A.* 1931, **25**, 5071. (10) C.Wagner, *ZPC* 1924, **113**, 261.

# OXIDATION-REDUCTION
## of compounds of different elements

*Liquid phase*

**Reductant:** Rare earth element

**Oxidant:** VI th group element

Amounts are in M/l.
Rates are in M/l per sec.

| No. | Reaction | Solvent | Ionic strength | Addend (catalyst) | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ Ce^{+++} + S_2O_8^{--} \rightarrow 2\ Ce^{++++} + 2\ SO_4^{--}$ | $H_2O$ | $\mu = 1.25$ | $Ag^+$ | $k\,B\,[Ag^+]$ | 25 | 4.9 | -3 | |
| | | | 2.95 | | | " | 4.3 | -3 | |
| | | | 1.5 | " | " | 35 | 7.5 | -3 | |
| | | | 3 | | | " | 7.6 | -3 | ~ 10 |

## COMMENTS

Rate determining step $Ag^+ + S_2O_8^{--} \rightarrow Ag^{+++} + 2\ SO_4^{--}$, see 732.160.

## LITERATURE

W. H. Cone, *ACS* 1945, **67**, 78.



National Bureau of Standards - National Research Council

May, 1950

# OXIDATION-REDUCTION

*Liquid phase*

## of compounds of different elements

**Reductant:** VIII th group element

**Oxidant:** VII th " "

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Ionic strength | Defined mass - action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ Fe^{++} + I_2 \rightarrow 2\ Fe^{+++} + 2\ I^-$ (nitrates) | $H_2O$ | | $-dA/dt = r_1 + r_2$ <br> $r_1 = (k_4AB + k_6A[I_3^-])/[1 + L\ (m_4 + m_6M)/A]$ | | | | See 732.780 | |
| | | | $\mu =$ 0.09 | | 25 | $k_4$ 1.5 | -4 | | |
| | | | | | | $k_6$ 2.4 | -4 | | |
| | | | | | | $m_4$ 1.8 | -2 | | |
| | | | | | | $m_6$ 2.0 | +1 | | |
| | | | 0 | | | $k_4$ 2.4 | -4 | | |
| | | | | | | $k_6$ 5.8 | -4 | | |
| | | | | | | $m_4$ 2.8 | -1 | | |
| | | | | | | $m_6$ 7.5 | +1 | | |
| | | | | $r_2 = (k'_4AB/M[H^+])/(1 + Lm'/A[H^+])$ | | | | | |
| | | | 0.09 | | | $k'_4$ 1.7 | -9 | | |
| | | | | | | $m'$ 1.4 | -3 | | |
| | | | | | | $K$ ~ 1 | +4 | | |
| | | | 0 | | | $k'_4$ 1.1 | -9 | | |
| | | | | | | $m'$ 3.4 | -3 | | |
| | | | | | | $K$ ~ 1.5 | +5 | | |
| | (at low $[I^-]$, buffer, $[H^+] = 0.02 - 0.0025$) | | 0.055 | $-dA/dt = (k'_4AB/M[H^+])/(1+m\ A/M[H^+])$ (initial rate) | | $k'_4$ 1.3 | -9 | | |
| | | | | | | $m$ 2.8 | -9 | | |

## COMMENTS

Notation, Mechanism, see reverse reaction 732.780.

## LITERATURE

See 732.780.

# OXIDATION-REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** Organic compound

**Oxidant:** ozone

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $HCOOH + O_3 \rightarrow CO_2 + O_2 + H_2O$ | $H_2O$ | $10^4$ A = | $10^4$ B = | $HClO_4$ | 0.1 | $-dA/dt = k\,AB$ | | | |
| | | | 25.6 | 16.3 | $\mu$ = 0.1 | | | 0 | 1.3 | -1 |
| | | | 8.2 | 5.6 | | | | " | 1.2 | -1 |
| | | | 2.05 | 14.4 | | | | " | 9.0 | -2 |
| | | | 0.99 | 16.3 | | | | " | 5.3 | -2 |
| | | | | | $HClO_4$ | 0.03 | " | | | |
| | | | 2.93 | 18.4 | $\mu$ = 0.1 | | | " | 3.4 | -1 |
| | | | " | 19.8 | + $Cl^-$ | $1.8 \times 10^{-5}$ | | " | 2.0 | -1 |
| | | | " | 18.9 | " | $3.6 \times 10^{-5}$ | | " | 2.0 | -1 |
| | | | " | 19.4 | " | $3.0 \times 10^{-3}$ | | " | 1.75 | -1 |
| | | | " | 20.4 | $CH_3COOH$ | $4.0 \times 10^{-4}$ | | " | 2.2 | -1 |
| | | | " | 18.2 | " | $8.0 \times 10^{-4}$ | | " | 1.9 | -1 |
| | | | " | 15.5 | " | $1.0 \times 10^{-2}$ | | " | 1.6 | -1 |
| | | | | | $HClO_4$ | 0.01 | | | | |
| | | | | | $\mu$ = 0.1 | | | | | |
| | | | 2.10 | 17.4 | + $Cl^-$ | $1. \times 10^{-4}$ | | " | 5.3 | -1 |
| | | | 4.2 | 17.5 | " | $1 \times 10^{-3}$ | | " | 5.3 | -1 |
| | | | 2.1 | 16.4 | $CH_3COOH$ | $8.0 \times 10^{-4}$ | | " | 5.3 | -1 |
| | | | 4.2 | 15.7 | " | $1.0 \times 10^{-2}$ | | " | 4.5 | -1 |

| No. | Reaction | Solvent | Amount of reactant | | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| .1.1 | $2\,O_3 \rightarrow 3\,O_2$ | $H_2O$ | $10^4A =$ | $10^4$ [HCOOH] | | | $-dA/dt = kA^2$ | | | |
| | | | | | $HClO_4$ | 0.1 | | | | |
| | | | 16.3 | 25.6 | $\mu =$ | 0.1 | | 0 | 1.2 | -1 |
| | | | 5.6 | 8.2 | | | | " | 1.05 | -1 |
| | | | 14.4 | 2.05 | | | | " | 5.9 | -2 |
| | | | 16.3 | 0.99 | | | | " | 4.5 | -2 |
| | | | 15.7 | 0.05 | | | | " | 1.4 | -2 |
| | | | 14.3 | 0.025 | | | | " | 9.0 | -3 |
| | | | | | $HClO_4$ | 0.03 | | | | |
| | | | 18.4 | 2.93 | $\mu =$ | 0.1 | | " | 2.3 | -1 |
| | | | 19.8 | " | $+ Cl^-$ | $1.8 \times 10^{-5}$ | | " | 5.5 | -2 |
| | | | 18.9 | " | " | $3.6 \times 10^{-5}$ | | " | 3.1 | -2 |
| | | | 20.4 | " | $CH_3COOH$ | $4.0 \times 10^{-4}$ | | " | 7.0 | -2 |
| | | | 18.2 | " | " | $8.0 \times 10^{-4}$ | | " | 4.0 | -2 |

## COMMENTS

Reaction (.1.1) accompanies the main reaction (.1). The mechanism is represented as $HCOOH \rightarrow HCOO^- + H^+$; $HCOO^- + O_3 \rightarrow OH + CO_2^- + H_2O$; $OH + O_3 \rightarrow HO_2 + O_2$; $HO_2 + O_3 \rightarrow OH + 2\,O_2$; the inhibition, $OH + CH_3COOH \rightarrow H_2O + CH_3COO$, and $H^+ + Cl^- + OH \rightarrow H_2O + Cl$.

## LITERATURE

H. Taube, *ACS* 1941, **63**, 2453.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** **Aliphatic organic compound**

**Oxidant:** **VI th group element**

Amounts are in /M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $2\ CH_3OH + 2\ S_2O_8^{--} \rightarrow 2\ HCHO + 4\ HSO_4^-$ | $H_2O$ | A = 0.5 - 1.5<br>B = 0.015 | | | $kA^{1/2}B^{3/2}$ | 79.8 | 1.4 | -2 | * | (1) |
| .2 | $COOHCOOH + S_2O_8^{--} \rightarrow 2\ CO_2 + 2\ H^+ + 2\ SO_4^{--}$ | $H_2O$ | A = 0.01; B = 0.005 | $Ag^+$ | $2 \times 10^{-5}$ | $kB\,[Ag^+]$ | 25 | ~ 4 | 0 | * | (2) |
| .3 | $3\ (CH_3)_2CHOH + 2\ CrO_3 + 6\ H^+ \rightarrow 3\ (CH_3)_2CO + Cr^{+++} + 6\ H_2O$ | $H_2O$ | A = 0.21; $10^3B$ = 5.5; $[H^+]$ = 0.31<br>" 1.1 "<br>0.03 5.5 "<br>0.21 " 0.11 | | | $kAB\,[H^+]$ | 40<br>"<br>"<br>" | 3.4<br>3.8<br>2.9<br>4.6 | -2<br>-2<br>-2<br>-2 | * | (3,4) |
| .3.1 | $3\ [(CH_3)_2CDOH(55\ \%) + (CH_3)_2CHOH(45\ \%)] + CrO_3 + 6\ H^+$ | $H_2O$ | A = 0.21; $10^3B$ = 5.5; $[H^+]$ = 0.31<br>" 1.1 "<br>0.03 5.5 "<br>0.21 " 0.11 | | | " | "<br>"<br>"<br>" | 1.8<br>2.0<br>1.5<br>2.45 | -2<br>-2<br>-2<br>-2 | * | " |

## COMMENTS

(.1) The reaction $2\ S_2O_8^{--} + H_2O \rightarrow 4\ HSO_4^- + O_2$ could be disregarded. Mechanism proposed: $S_2O_8^{--} + CH_3OH \rightarrow HSO_4^- + SO_4^{\cdot -} + CH_2OH^{\cdot}$; $SO_4^{\cdot -} + CH_3OH \rightarrow HSO_4^- + CH_2OH^{\cdot}$; $CH_2OH^{\cdot} + S_2O_8^{--} \rightarrow HSO_4^- + SO_4^{\cdot -} + HCHO$; $2\ CH_2OH^{\cdot} \rightarrow CH_3OH + HCHO$. (.2) $k$ about 500 times as great as in other $Ag^+$- catalyzed oxidations by $S_2O_8^{--}$. (.3) (.3.1) The ratio of the $k$ for the *pure* $(CH_3)_2CDOH$ and $(CH_3)_2CHOH$ is calculated to $k(.3.1)/k(.3) = 0.17 \pm 0.05$.

## LITERATURE

(1) P.D.Bartlett, J.D.Cotman, Jr., *ACS* 1949, **71**, 1419. (2) C.V.King, *ACS* 1928, **50**, 2089. (3) F.H.Westheimer, N.Nicolaides, *ACS* 1949, **71**, 25. (4) F.H.Westheimer, A.Novick, *JCP* 1943, **11**, 506.

# OXIDATION - REDUCTION

## of compounds of different elements

*Liquid phase*

**Reductant:** **Aliphatic organic compound**

**Oxidant:** **VII th group element**

Amounts are in M/l.

Rates are in M/l per sec.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .1 | $5\ HCOOH + 2\ HIO_3 \rightarrow 5\ CO_2 + I_2 + 6\ H_2O$ | $H_2O$ | A = 0.1 - 0.3 | $H_2SO_4$ | 0.01 - 0.3 | See reaction (.1.1) | | | | | * | ([2]) |
| .1.1 | $HCOOH + I_2 \rightarrow CO_2 + HI$ | " | A = 0.1 - 0.3; $I^-$ = 0.001 - 0.3 | $H_2SO_4$ | 0.01 - 0.3 | $k_1B[HCOO^-] = k_1'BA/[H^+]f^2$ | | | | | $*_a$ | |
| | | | | | | | 60 | | | | | |
| | | | | | | | $k_1$ | 1.7 | 0 | | | |
| | | | | | | | $k_1'$ | 2.5 | -4 | | | |
| | | " | " | " | " | $(k_2/f)[AB[IO_3^-][H^+](1 + aA)]$ | | | | | $*_b$ | |
| | | | | | | | 60 | | | | | |
| | | | | | | | $k_2$ | 3.3 | -4 | | | |
| | | | | | | | $a$ | 5.7 | 0 | | | |
| .2 | $COOHCOOH + Cl_2 \rightarrow 2\ CO_2 + 2\ Cl^- + 2\ H^+$ | $H_2O$ | A = 0.01 - 0.05; HCl = 0.1 - 0.5; | | | $kK[COOHCOO^-]B/[H^+][Cl^-]$ | | | | | * | ([7]) |
| | | | | | $\mu$ = | | 10 | | | | | |
| | | | | | 0.25 - 0.5 | | $k$ | 4.2 | 0 | | | |
| | | | | | " | | $kK$ | 1.85 | -3 | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .2 | $COOHCOOH + Cl_2 \rightarrow 2\ CO_2 + 2\ Cl^- + 2\ H^+$ *(continued)* | | | | $\mu =$ | | 15 | | | | | |
| | | | | | 0.25 - 0.5 | | $k$ | 6.55 | 0 | | | |
| | | | | | " | | $kK$ | 3.7 | -3 | | | |
| | | | | | 2 | | $k$ | 7.3 | 0 | | | |
| | | | | | " | | $kK$ | 4.0 | -3 | | | |
| | | | | | | | 20 | | | | | |
| | | | | | 0.25 - 0.5 | | $k$ | 1.05 | +1 | | | |
| | | | | | | | $kK$ | 7.35 | -3 | | | |
| | | | | | 0.7 | | $k$ | 1.15 | +1 | | | |
| | | | | | | | $kK$ | 7.7 | -3 | 15 | | |
| .2.1 | $COOHCOO^- + HClO \rightarrow 2\ CO_2 + Cl^- + H_2O$ | $H_2O$ | as (.2) | | | as (.2) | | | | | * | ([7]) |
| .3 | $COOHCOOH + Cl_2 \rightarrow 2\ CO_2 + 2\ Cl^- + 2\ H^+$ | $H_2O$ | $HCl = 2$; $[Mn^{++}] = 0.01$ | $Mn^{+++}$ | $10^4[Mn^{+++}]$ | $k\ [Mn^{+++}]$ | | | | | * | ([17]) |
| | | | $10^2B \sim 0.6 - 0.7$; $10^2A = 0.5 - 1$ | | 0.27 - 0.6 | | 25.2 | 1.4 | -1 | | | |
| | | | 0.16 | | 0.27 | | " | 1.2 | -1 | | | |
| | | | 0.10 | | " | | " | 9.7 | -2 | | | |
| | | | 0.03 | | " | | " | 4.8 | -2 | | | |
| | | | 0.016 | | " | | " | 2.7 | -2 | | | |
| | | | $\sim 0.5 - 1.0$; 0.8 - 8.0 | | 0.11 - 0.27 | | 34.7 | 3.7 | -1 | | | |
| | | | 0.42 0.16 | | 0.11 | | " | 2.9 | -1 | | | |
| | | | 0.47 0.03 | | " | | " | 1.4 | -1 | | | |
| .3.1 | $MnC_2O_4^+ \rightarrow Mn^{++} + C_2O_4^-$ | | See (.5.2) | | | | | | | | | |

| No. | Reaction | Solvent | Amount of reactant | | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .4 | $COOHCOOH + Cl_2 \rightarrow$ | $H_2O$ | A = | ;$10^2$B = | $Fe^{+++}$; | $+ d[Fe^{+++}]/dt = R$ | | | | | | * | (16) |
| | $2\ CO_2 + 2\ Cl^- + 2\ H^+$ | | 0.2 | 1.7 | | $R = 6.7 \times 10^{-6}$ | $kAR^{1/2}$ | 25 | 5.2 | -2 | | | |
| | | | " | 0.7 | | $5.1 \times 10^{-5}$ | | " | 3.1 | -2 | | | |
| | | | " | " | | $9.2 \times 10^{-9}$ | | " | 5.2 | -2 | | | |
| | | | 0.02 | " | | $1.6 \times 10^{-7}$ | | " | 5.0 | -2 | | | |
| | | | 0.007 | 0.14 | | $6.0 \times 10^{-8}$ | | " | 5.2 | -2 | | | |
| | | | 0.39 | 0.11 | | $1.85 \times 10^{-7}$ | $k'(ABR)^{1/2}$ | 25 | 7.15 | -1 | | | " |
| | | | " | 0.06 | | " | | " | 7.15 | -1 | | | |
| | | | 0.2 | 0.05 | | $3.7 \times 10^{-8}$ | | " | 7.3 | -1 | | | |
| .5 | $COOHCOOH + 2\ Mn^{+++} \rightarrow$ | $H_2O$ | | | | | $kB$; $k = k_1 + (k_2[H^+]/A)$ | | | | | | (6) |
| | $2\ CO_2 + 2\ Mn^{++} + 2\ H^+$ | | | | | | | 14 | | | | | |
| | | | | | | | | $k_1$ | 4.0 | -4 | | | |
| | | | | | | | | $k_2$ | ~ 8 | -4 | | | |
| | | | | | | | | 20 | | | | | " |
| | | | | | | | | $k_1$ | 8.5 | -4 | 25 | | |
| | | | | | | | | $k_2$ | ~ 1.4 | -3 | | | |
| .5.1 | $COOHCOOH + 2\ Mn^{+++} \rightarrow$ | $H_2O$ | | | $kB$; $k = [2\ k_1/(1 + b + c)] + 2\ k_2/(1 + b + c)] + [2\ k_3 c/(1 + b + c)]$ | | | | | | | | |
| | $2\ CO_2 + 2\ Mn^{++} + 2\ H^+$ | | $(COOH)_2$ | = 0.05 - 0.15 | | | | 25.2 | | | | * | (18) |
| | | | $[C_2O_4^{--}]$ | = 0.02 - 0.08 | | $\mu = 2$ | | $k_1$ | 1.95 | -1 | 18.3 | | |
| | | | HCl | = 0.1 - 0.4 | | | | $k_2$ | 7.7 | -4 | | | |
| | | | $(COOH)_2$ | = 0.02 - 0.44 | | | | $k_3$ | 3.3 | -4 | 22.2 | | |
| | | | $[C_2O_4^{--}]$ | = 0.08 - 0.2 | | $\mu = 0.65$ | | | | (18 - 36°C) | | | |
| | | | $Mn^{++}$ | = 0.05 | | | $b = 4.02 \times 10^6 [C_2O_4^{--}]$ | | | | | | |
| | | | | | | | $c = 2.87 \times 10^9 [C_2O_4^{--}]^2$ | | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^o \times 10^n$ $k^o$ | $n$ | $E$ | Comments | Literature |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .5.2 | $MnC_2O_4^+ \rightarrow Mn^{++} + C_2O_4^-$ | $H_2O$ | | | | $k_1A$ | 15.0 | 5.85 | -2 | | * | (17) |
| | | | | | | | 25.2 | 1.95 | -1 | | | (18) |
| | | | | | | | 34.7 | 4.80 | -1 | 18.3 | | |
| .5.3 | $Mn(C_2O_4)_2^-$ $\rightarrow Mn^{++} + C_2O_4^- + 2\ C_2O_4^{--}$ | $H_2O$ | | | | $k_2A$ | 25.2 | 7.7 | -4 | | * | (18) |
| .5.4 | $Mn(C_2O_4)_3^{---}$ $\rightarrow Mn^{++} + C_2O_4^- + 2\ C_2O_4^{--}$ | $H_2O$ | | | | $k_3A$ | 25.2 | 3.3 | -4 | 22.2 | * | (18) |
| .6 | $5\ C_2O_4^{--} + 2\ MnO_4^- + 16\ H^+$ $\rightarrow 10\ CO_2 + 2\ Mn^{++} + 8\ H_2O$ | $H_2O$ | See Comments | | | | | | | | | |

## COMMENTS

**(.1) (.1.1)** Reaction (.1) proceeds over (.2.1), followed by $5\ HI + HIO_3 \rightarrow 3\ I_2 + 3\ H_2O$ (see 722.770). Reaction (.1.1) may proceed over two paths. For the direct path *(a)*, $k_1 = k_1'/K$, where $K = [HCOO^-][H^+]/[HCOOH] = 1.55 \times 10^{-4}$ at 60°C; temperature coefficient near 55°C, 2.78. The indirect path *(b)* is $I_2 + H_2O \rightleftarrows HIO + HI$; $HCOOH + HIO \rightarrow CO_2 + HI + CO_2$; the total rate approaches *(b)* when $[IO_3^-]$ and $[H^+]$ are large and $[I_2]$ is small; $f$ = activity coefficient of HCOOH. **(.2) (.2.1)** Reaction (.2) proceeds over the equilibrium $Cl_2 + H_2O \rightleftarrows HClO + H^+ + Cl^-$ ( at $\mu = 0$, $10^4K = 2.58, 3.28, 4.06$, at 10°, 15°, 20°C), followed by the rate determining step (.2.1). $[COOHCOO^-]$ from the first dissociation constant $\log K_1 = \bar{2}.756 + 0.42\mu^{1/2} - 0.275\mu$. **(.3) (.3.1)** The mechanism of the reaction is represented as

## COMMENTS *(continued)*

$COOHCOOH + Mn^{+++} \rightleftharpoons MnC_2O_4^+ + 2\,H^+$; $COOHCOOH + MnC_2O_4^+ \rightleftharpoons Mn(C_2O_4)^- + 2\,H^+$; (.3.1) $MnC_2O_4^+ \rightarrow Mn^{++} + C_2O_4^-$, rate determining, which see under (.5.2). (.4) $Fe^{+++}$ is added at the rate $R$ (M/l per sec, converted from M/l per min). The rate constants $k$ and $k'$ (converted from min to sec) are, with respect to time, obviously of the dimension $(\text{time})^{-1/2}$. The reaction is represented as a chain reaction, following a scheme $COOHCOOH \rightleftharpoons HC_2O_4^- + H^+$ ($K$); $Fe^{++} + Cl_2 \rightarrow FeCl^{++} + Cl$ ($k_1$); $HC_2O_4^- + Cl \rightarrow H^+ + Cl^- + C_2H_4^-$ ($k_2$); $C_2O_4^- + Cl_2 \rightarrow Cl + Cl^- + 2\,CO_2$ ($k_3$); $Cl + C_2O_4^- \rightarrow Cl^- + 2\,CO_2$ ($k_4$); $Cl + Cl \rightarrow Cl_2$ ($k_5$); $k = k_2K/k_5^{1/2}([H^+] + K)$; $k' = (k_2k_3/2\,k_4)^{1/2}(K/(K + [H^+]))^{1/2}$. The reaction is inhibited by $NH^+$, $NO^{++}$, $Mn^{++}$, $Ce^{+++}$. Further data, and chain length computations, see original ([16]).

(.5.1) (.5.2) (.5.3) (.5.4) For empirical first-order constants ($k$B) of reaction (.5.1), see original ([18]). This reaction is representable by the succession of reactions (.5.2) (.5.3) (.5.4), followed by the rapid step $Mn^{+++} + C_2O_4^- \rightarrow Mn^{++} + 2\,CO_2$. The coefficients of $b$ and $c$ are ratios of equilibrium constants (see in original). – Reaction (.5.2) is also the rate determining step for (.3). (.6) No single rate equation possible. For proposed mechanisms, including the the steps of (.5.1) [(.5.2) (.5.3) (.5.4)] see ([15]) ([10]) ([8]) ([9]) ([5]) ([3]) ([17]) ([18]) ([6]) ([11]). Newer mechanism proposed by ([1]).

## LITERATURE

([1]) E.Abel, *MHC* 1949, **80**, 461. ([2]) E.Abel, A.Bilderman, *MHC* 1936, **68**, 215.
([3]) J.Bradley, G.van Praagh, *CSL* 1938, 1624. ([4]) W.C.Bray, J.B.Ramsey, *ACS* 1933, **55**, 2279.
([5]) G.H.Cartledge, W.P.Ericks, *ACS* 1936, **58**, 2061. ([6]) F.R.Duke, *ACS* 1947, **69**, 2885.
([7]) R.O.Griffith, A.McKeown, *TFS* 1932, **28**, 518. ([8]) H.F.Launer, D.M.Yost, *ACS* 1934, **56**, 2571.
([9]) O.M.Lidwell, R.P.Bell, *CSL* 1935, **57**, 1303. ([10]) F.O.Oberhauser, W.Hensinger, *BDC* 1928, **61**, 521.
([11]) M.J.Polissar, *JPC* 1935, **39**, 1057. ([12]) J.B.Ramsey, E.L.Colichman, L.C.Pack, *ACS* 1946, **68**, 1695. ([13]) J.B.Ramsey, R.Sugimoto, H.Devorkin, *ACS* 1941, **63**, 3480.
([14]) A.Skrabal, *ZAC* 1904, **42**, 1 and 1910, **68**, 48. ([15]) H.Taube, *ACS* 1946, **68**, 611.
([16]) H. Taube, *ACS* 1947, **69**, 1418. ([17]) H.Taube, *ACS* 1948, **70**, 1216.



☆U. S. GOVERNMENT PRINTING OFFICE : O—1951

DEPARTMENT OF COMMERCE
UNITED STATES OF AMERICA

Buckman Bindery, Inc.
Manchester, Ind.
MAY 1954
Do Not Please